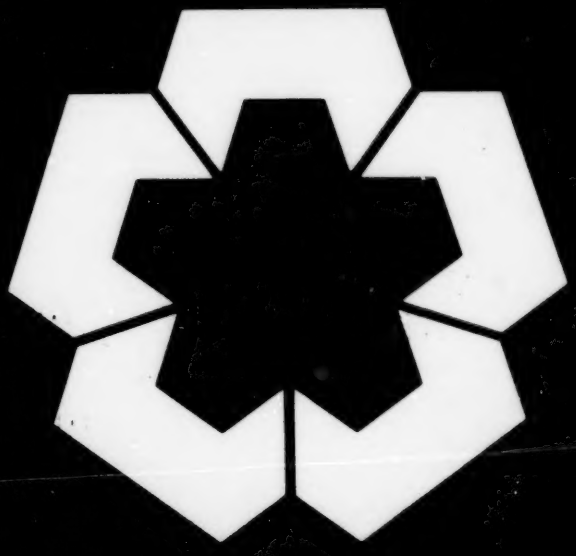

Athabasca Oil Sands Precipitation Chemistry Studies: 1976 79 and 1981

AOSERP Report 129

Alberta

E R R A T A

AOSERP REPORT 129

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ATHABASCA OIL SANDS PRECIPITATION CHEMISTRY STUDIES: 1976-79 and 1981

AOSERP Report 129

Alberta
ENVIRONMENT
Research Management Division
14th Floor, Standard Life Centre
10405 Jasper Avenue
Edmonton, Alberta, Canada
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ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM
RESEARCH REPORTS

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Athabasca Oil Sands Precipitation Chemistry Studies:
1976-79 and 1981

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The Hon. J.W. (Jack) Cookson
Minister of the Environment
222 Legislative Building
Edmonton, Alberta

Sir:

Enclosed is the report "Athabasca Oil Sands Precipitation Chemistry Studies: 1976-79 and 1981".

This report was prepared for the Research Management Division through the Alberta Oil Sands Environmental Research Program.

Respectfully,

W. Solodzuk, P. Eng.
Deputy Minister, Alberta Environment

This report is made available as a public service. The Department of Environment neither approves nor disagrees with the conclusions expressed herein, which are the responsibility of the authors.

ATHABASCA OIL SANDS PRECIPITATION CHEMISTRY STUDIES: 1976-79 and 1981

by

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for

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AOSERP Report No. 129

June 1982

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ABSTRACT

A study of the wet deposition of atmospheric pollutants in northeastern Alberta was initiated by Alberta Environment and Atmospheric Environment Service in 1976. The objectives of this on-going study are to determine changes in the input rate of atmospheric trace substances into sensitive ecosystems and to provide a data base for the documentation of variations in the chemical characteristics of precipitation.

In 1980, scientists from Research Management Division, Alberta Environment conducted an extensive review of the procedures and techniques which were being used in other precipitation chemistry studies. This resulted in the identification of potential inconsistancies in the existing data base. These problem areas were attributed to sample collection procedures, restrictions of the chemical analyses techniques and the reliability of the data with only a limited quality assurance program.

Many of these concerns have been addressed in the 1981 precipitation chemistry field season. Alberta Environment introduced changes in the methodology that would both minimize the possibility of non-representative samples and ensure that the data would be comparable to other precipitation chemistry studies.

ACKNOWLEDGEMENTS

We would like to thank our colleagues at Research Management Division and Alberta Environmental Centre for their comments and assistance. In particular, Ms. Bonnie Magill, Air System, RMD, Dr. Yan Lau, Pollution Control Division, Alberta Environment and Mr. A.S. Mann, Atmospheric Environment Service, provided valuable suggestions, for which we are grateful.

1. INTRODUCTION

In 1976 a study of atmospheric pollutants was initiated by Alberta Environment and Atmospheric Environment Service. It involved the collection and analyses of event rain samples taken from the Athabasca Oil Sands region of northeastern Alberta. The objectives of the study were to determine changes in the input rate of atmospheric trace substances into sensitive ecosystems and to provide a data base for the documentation of variations in the chemical characteristics of precipitation. The concern was that these parameters would change in space and time as a result of additional atmospheric contaminant sources (Barrie et al.1978).

The fundamental purpose of precipitation chemistry studies should be to generate accurate data sets that can be merged with present and future research. However, there are a variety of collection procedures, sampling devices, and analytical techniques utilized in the study of precipitation chemistry. These variations in methodologies may not provide reliable data bases for the purposes of inter-study comparisons or evaluation of trends in the chemical composition of precipitation (Jansen 1981). The main causes of these problems include:

1. Influence of collector design in obtaining a representative precipitation sample;
2. Geochemical and biological changes which occur within the sample container once the sample has been collected;
3. Effects of storage on sample integrity;
4. Leaching or absorbtion of substances from or to the collector surface;
5. Sampling site characteristics;
6. Variations in sampling intervals;
7. Differences between field and laboratory chemistry measurements; and
8. Background error (Galloway and Likens 1976; Parkhurst et al. 1980).

In 1980, scientists from Research Management Division, Alberta Environment conducted an extensive review of the procedures and techniques being used in other precipitation chemistry studies. This resulted in the identification of potential inconsistancies in the 1976-79 data base from the Alberta Oil Sands Environmental Research Program (AOSERP) precipitation chemistry studies (Peters 1981a, b; Peters et al. 1981). These problem areas were attributed to sample collection procedures, restrictions of the chemical analyses techniques and the reliability of the data with only a limited quality assurance program.

To address these concerns sampling techniques and procedures used by Ministry of Environment, Ontario were adopted for use in the Athabasca Oil Sands region. There were several justifications for this: (1) Ontario has had more experience than most other governments in the investigation of precipitation chemistry, and (2) Ontario's sampling procedures and chemical analyses techniques had successfully been evaluated in terms of comparison to other precipitation chemistry methodologies. More importantly, the fundamental objectives of Alberta Environment's study coincided with those of Ontario Environment: (1) to minimize sample contamination; (2) maximize collection efficiency; and (3) maintain high quality control on the network operations (Vet and Chan 1980; Vet 1980a, b, c).

In the following sections the techniques and procedures which were used in the pre-1981 and 1981 precipitation chemistry field studies will be compared and contrasted. Also, the reliability and accuracy of the resultant data will be assessed in terms of the methodologies employed in these studies.

2. THE ATHABASCA OIL SANDS STUDY AREA

The study area is in northeastern Alberta (Figure 1). It is the main site of Alberta's tar sands industries and includes much of the evaluated Oil Sands reserves in the province.

The vegetation and soils are characteristic of the boreal forest region of northern Canada. This forest is a mosaic of aspen, pine and white spruce stands interspersed with willow and black spruce. Fire has played a dominant role in shaping the mixedwood nature of the forest (La Roi 1967).

The surficial deposits of the lowland areas adjacent to the rivers are mainly composed of glacial outwash, lake deposits and wind-blown materials. The higher elevations, such as Birch, Stoney and Muskeg Mountains, are primarily glacial tills (Atlas of Alberta 1967).

Northern Alberta is associated with the mid-Alberta storm track. It brings precipitation to the area between May and September. The average precipitation during this period ranges from about 350 to 520 mm with July being the wettest month. The mean summer temperatures are 10.5 to 14.0^{o}C throughout the region. Differences in elevation and latitude are the major climate controls which influence these variations in temperature and precipitation (Longley and Janz 1978).

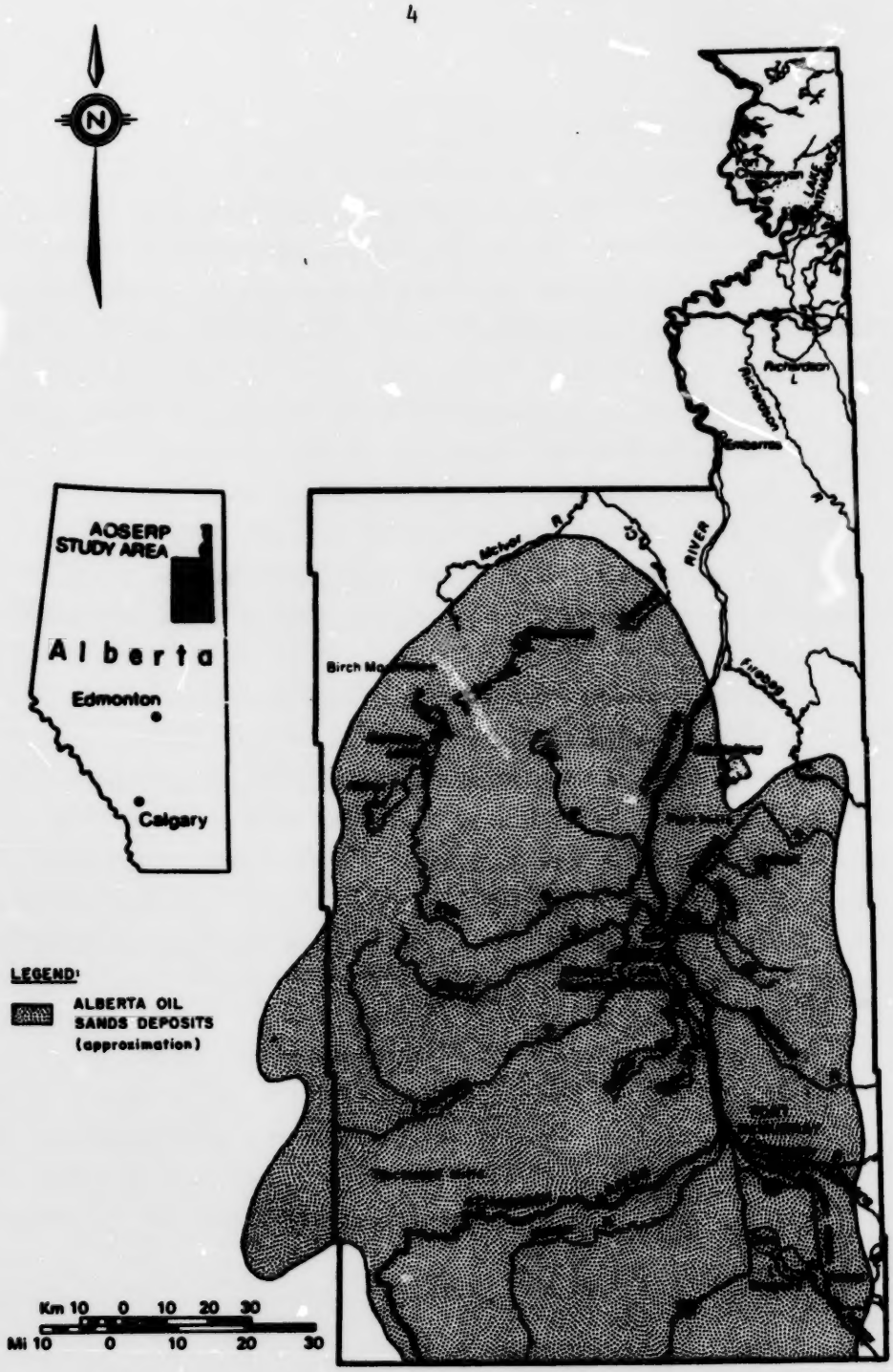


FIGURE 1: AOSERP (Athabasca Oil Sands) STUDY AREA

3. SUMMER PRECIPITATION CHEMISTRY FIELD STUDIES: 1976-79 and 1981

Methodologies and results of the pre-1981 precipitation chemistry field studies in the Athabasca Oil Sands area have been published elsewhere. For a detailed account of these studies the reader is referred to Nespliak (1977), Barrie et al. (1978), and Peters et al. (1981).

3.1 THE PRECIPITATION CHEMISTRY NETWORK

The Athabasca Oil Sands area has unique characteristics for the study of precipitation chemistry: (1) the emissions from the 2 proximal point-sources are quantifiable, and (2) there are no major upwind emission sources.

3.1.1 1976-79 Studies Network

There are many factors which affect the selection of sites for the precipitation chemistry samplers. Two criteria were considered for locating the sampling sites when the 1976-79 summer precipitation chemistry network was being set up. The sites had to be manned during each May to September period and be radially dispersed from the two emission sources in the Oil Sands region. The forest fire lookout sites of the Alberta Forest Service (A.F.S.), the Oil Sands Mildred Lake Research Facility and the Steepbank River stream gauging site met these two prerequisites. In all, 14 A.F.S. lookout tower sites in north-eastern Alberta were utilized (Table 1 and Figure 2). At these sites the samplers were placed alongside the meteorological instruments and shelters of the A.F.S. climatological network.

3.1.2 1981 Study Network

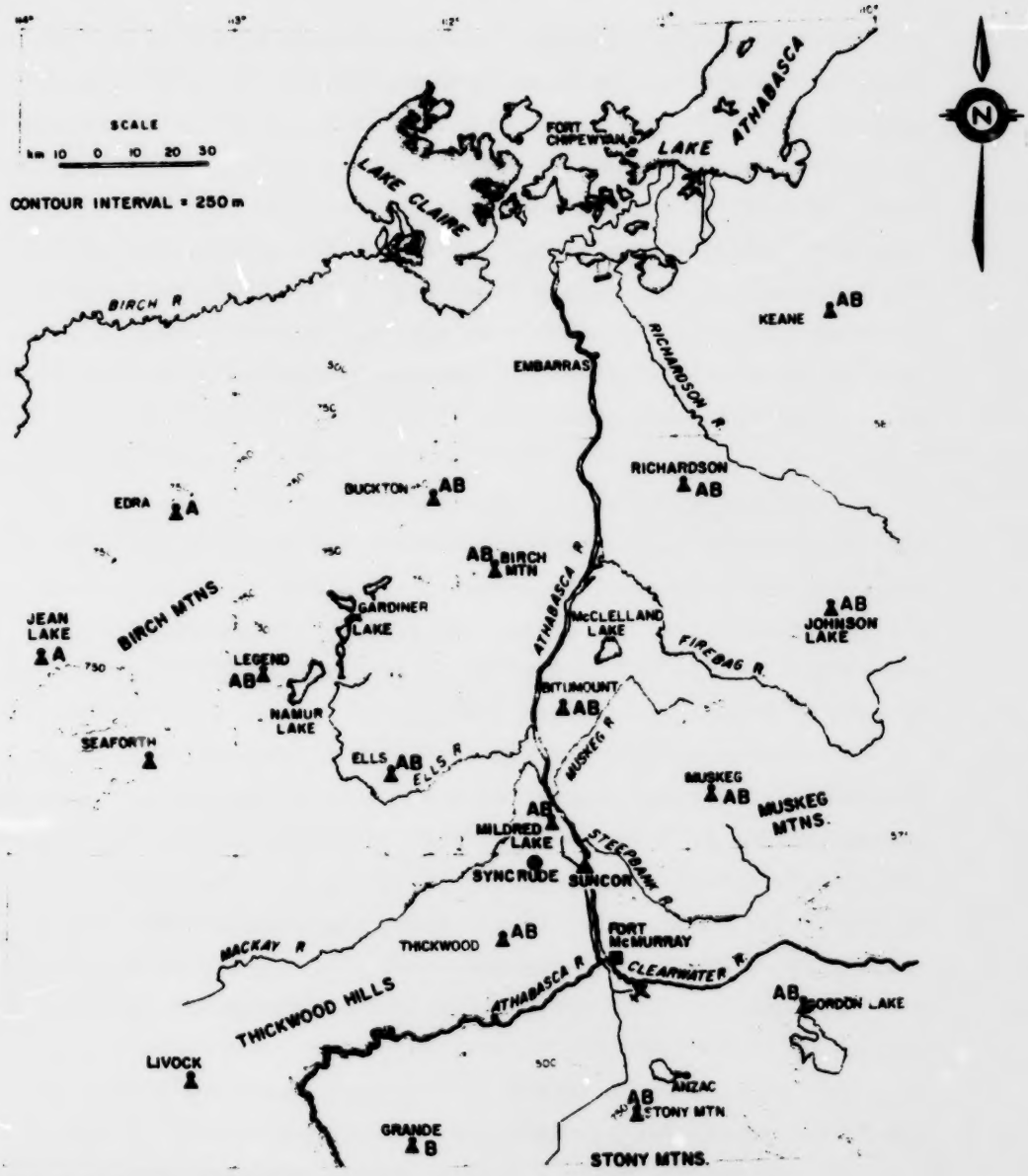
The most important parameters to consider for site selection are the fulfilment of network objectives and the prevention of sample contamination by sources other than those being studied. These factors were examined when the 1981 network was being planned.

Table 1. Precipitation event sampling site locations for 1976-79 and 1981 studies.

Site	Location		Elevation (m.a.s.l.)[b]	Years in Operation	
	Lat.	Long.		1976-79	1981
Birch Mtn. Lo.[a]	57° 43'	111° 51'	850	☐	☐
Bitumont Lo.	57° 22'	111° 32'	350	☐	☐
Buckton Lo.	57° 52'	112° 06'	790	☐	☐
Edra Lo.	57° 51'	113° 15'	790	☐	
Ells Lo.	57° 07'	112° 21'	560	☐	☐
Gordon Lo.	56° 37'	110° 30'	490	☐	☐
Grande Lo.	56° 18'	112° 13'	530		☐
Jean Lake Lo.	57° 30'	113° 53'	700	☐	
Johnson Lake Lo.	57° 35'	110° 20'	550	☐	☐
Keane Lo.	58° 19'	110° 17'	460	☐	☐
Legend Lo.	57° 27'	112° 53'	850	☐	☐
Mildred Lake	57° 05'	111° 35'	310	☐	☐
Muskeg Mtn. Lo.	57° 08'	110° 54'	550	☐	☐
Richardson Lo.	57° 53'	111° 02'	300	☐	☐
Steepbank River	56° 59'	111° 22'	270	☐	
Stoney Mtn. Lo.	56° 23'	111° 14'	760	☐	☐
Thickwood Hills Lo.	56° 47'	111° 45'	520	☐	☐

[a] Lo. = Lookout

[b] m.a.s.l. = metres above sea level



PRECIPITATION SAMPLING STATIONS:
A - 1976 - 1979
B - 1981

EMISSION SOURCES
● - SYNCRUDE
▲ - SUNCORE

A - ALBERTA FOREST FIRE LOOKOUT TOWER

FIGURE 2: PRECIPITATION EVENT SAMPLING SITES

3.1.2.1 Network objectives. One of the objectives of the 1981 study was to monitor the level of background pollutants in north-eastern Alberta. This required having samplers at several distances and directions from the industrial emission sources. The sampler locations used in the pre-1981 studies met these criteria because they were radially distributed and at various distances away from the pollutant sources (Table 1 and Figure 2). Therefore, depending on the trajectory of the air mass and the low-level winds, one or more of the stations would be measuring background concentrations on any particular occasion.

3.1.2.2 Sampling sites and local sources of contamination. Site specific characteristics were considered for potential sources of contamination. However, it is extremely difficult to eliminate all the sources that can affect the quality of the sample. They may be as close to the sampler as a few centimeters, to as far away as tens of kilometers (Jansen 1981).

An ideal site for precipitation collection is one that is located in a relatively secluded spot which is open, flat, grassed-in and surrounded by trees that are 200 m from the sampler (Vet and Chan 1980). It was nearly impossible to satisfy these criteria at every site in the study area. Thus, there was a trade off between those factors which influence the chemical integrity of the sample and those which affect the logistics and operations of the sampling units.

Factors which affect the chemical integrity of the precipitation samples at the forest fire lookout sites include:

1. Nearby trees - organic debris, throughfall and splash;
2. Buildings - splash, emissions;
3. Overhead wires - splash;
4. Ground cover - dry deposited wind blown contaminants; and
5. Surrounding topography - wind swept ridges, eddy zones.

Ontario Environment regards surrounding topography and ground cover to be the most important factors to consider when setting up a sampling network. In fact, a potential sampling site would be rejected if the ground cover and surrounding topography were not ideal. However, the criterion of nearby trees and buildings being at least 200 m away can be relaxed as long as the sampler is located at a distance of 2 1/2 times their height.

The actual locations of the samples in relation to site specific characteristics are illustrated in Appendix 8. The guy wires which support the lookout towers are not mapped. They extend about 15 to 25 m out from each corner of the towers.

3.2 PRECIPITATION SAMPLING INSTRUMENTATION AND PROCEDURES

3.2.1 1976-79 Studies

Three different designs of samplers were utilized in the pre-1981 surveys:

1. Event, wet-only samplers - these units were exposed to deposition from individual rain events only. All dry deposition, except that which occurred during the actual precipitation event, was excluded with these samplers;
2. Monthly bulk, wet-only samplers - these were exposed to the atmosphere during all rain events throughout each month. Again, dry deposition was reduced to a minimum; and
3. Monthly bulk, wet and dry samplers - these instruments were continually open to all forms of deposition during each month. They collected precipitation, particulates and some gases (Jansen 1981).

3.2.1.1 Event, wet-only samplers. The event, wet-only sampling apparatus illustrated in Figure 3 was used at the 15 manned sites in 1976 and 1977. Each consisted of a pointed metal rod to which

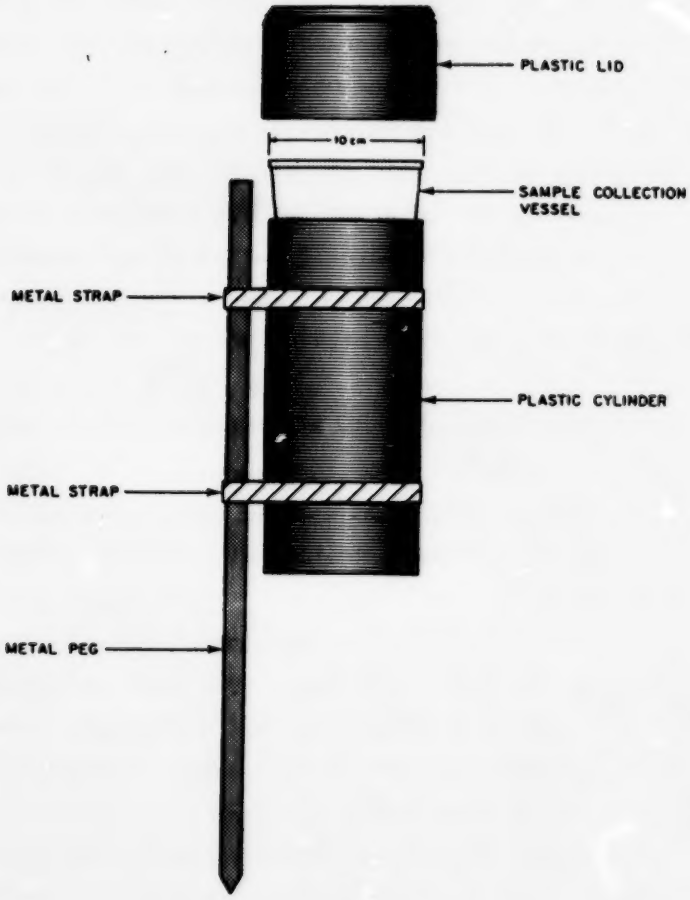


FIGURE 3 : EVENT, WET-ONLY SAMPLER

a 10 cm (diameter) x 25 cm plastic cylinder was attached. A second cylinder fit snugly into this one. A squat, pail-like plastic lid was used to cover the tops of both cylinders. The innermost cylinder served as the sample collection vessel.

The lid was removed to collect the precipitation sample when it began raining or when there appeared to be a good possibility of it starting to rain. The lid was taken off shortly before it rained because it was thought that the best chemical "washout" occurred at the beginning of the rain event (Nespliak 1977). Additionally, the forest tower operators had to be in their tower if thunderstorms were approaching or in their vicinities. After the rain event the samples were removed and poured into 250 mL polyethylene bottles and then stored in a refrigerator. They were picked up for transport to the Mildred Lake Research Facility at the end of each month.

There were several difficulties encountered with the use of this design of precipitation sampler:

1. Events of at least 10 mm were required to obtain sufficient volume for the chemical analyses. If the precipitation events deposited less than this the sample would have to be rejected;
2. The cylindrical rain catcher had to be meticulously washed and rinsed with laboratory detergent and distilled water. There was a large potential for contamination of the container during this process; and
3. The timing of the removal of the lid was not standardized among the operators.

During the 1978 and 1979 field seasons a potential source of contamination was eliminated. Instead of collecting the sample in the plastic cylinder the precipitation was directed into a 250 mL polyethylene bottle. A plastic funnel was used to channel the flow into the bottle. This removed the need to wash and rinse the cylindrical collection vessel, but the funnel now had to be cleansed between use and the possibility existed that it could be contaminated.

3.2.1.2 Monthly bulk, wet-only samplers. Monthly bulk, wet-only precipitation samples were collected at 4 sites using automated Finnish instruments (Figure 4). These units are capable of sensing precipitation. When the event was detected the sensor activated a movable hood which exposed a sample collection vessel to the atmosphere. When the precipitation abated the vessel was once again sealed by the hood.

The collection vessel was essentially a bucket with a plastic bag inside. The bag was folded over the rim and taped to the outer edge of the bucket. At the end of each month the bags were removed and constricted at the top to reduce evaporation and contamination. The samples were then transported to Mildred Lake where they were subsequently transferred to polyethylene bottles and refrigerated.

There were factors which limited the use of these samplers and because of these difficulties the Finnish precipitation collectors were only used during Summer 1976. Problems developed with the seal between the top of the collection vessel and the underside of the hood. A tight seal is important for preventing evaporative losses and contaminants from entering the vessel. Vet and Chan (1980) found that this condition is critical in preventing metals contamination of the sample. This arises from the constant recirculation of sample water as it evaporates inside the bucket, condenses on the underside of the hood and eventually drips back into the sample. Another problem was that an AC electric source was required to power the unit.

3.2.1.3 Monthly bulk, wet and dry sampler. This sampling device was a modified Sacramento storage rain gauge. A polyethylene bag served as the collection container within the storage rain gauge. The top of the bag was folded over the rim of the gauge. The bag was constricted near its top to reduce evaporation and prevent relatively large objects from entering the vessel.

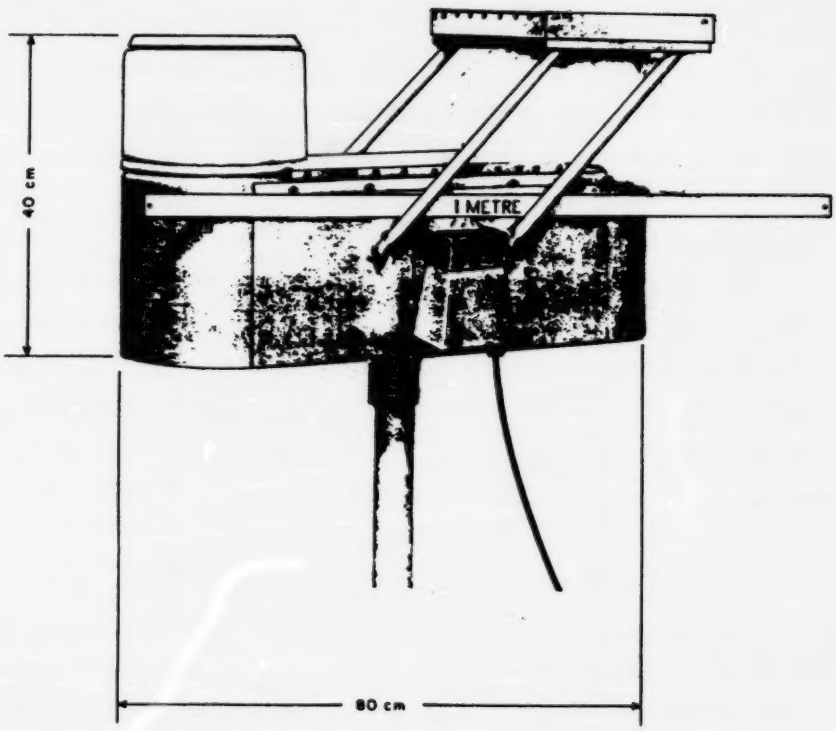


FIGURE 4: MONTHLY BULK, WET ONLY FINNISH PRECIPITATION COLLECTOR

This design of sampler was used at 4 sites during the 1976 study. However, it was not employed in future years because of its inherent limitation; the potential for contamination was much too great.

3.2.2 1981 Study

Event, wet-only sampling was the only form of precipitation collection during the 1981 study. The samplers used in the last year of the pre-1981 AOSERP studies were discarded in favor of a design similar to the one used by Ontario Environment. The new samplers were set up at 13 A.F.S. forest fire lookout towers and at Mildred Lake Research Facility in April 1981 (Table 1 and Figure 2).

The 1981 sampler design is illustrated in Figure 5. It consists of a 100 L (22 imp. gal.) polyethylene container (commonly used as a domestic refuse receptical) with a tight-fitting lid to prevent dry deposition from entering during non-precipitation events. Modified, polyethylene food processing bags were used inside the container to collect the sample. Two long stakes held the sampler firmly to the ground.

One of the few differences between these samplers and those of Ontario Environment is that Ontario uses a "knife-edge" collar around the rim of the container. This prevents raindrop splash from entering and reduces the amount of settling of particulates on the edge. However, the lip on the cover of Alberta Environment's samplers serves the same function.

The polyethylene sample collection bags have a heat-imprinted diagonal seam. This serves to funnel the precipitation into a lower compartment within the bag (Figure 6). The purpose of this was to reduce evaporative losses and to help prevent contamination of the sample. In addition, the bags were sealed by heat-imprinting once the samples were collected. They were then stored in black plastic bags and refrigerated until they were picked up.

The operators wore disposable plastic gloves whenever they handled the sampling equipment or sample bags. The manual of

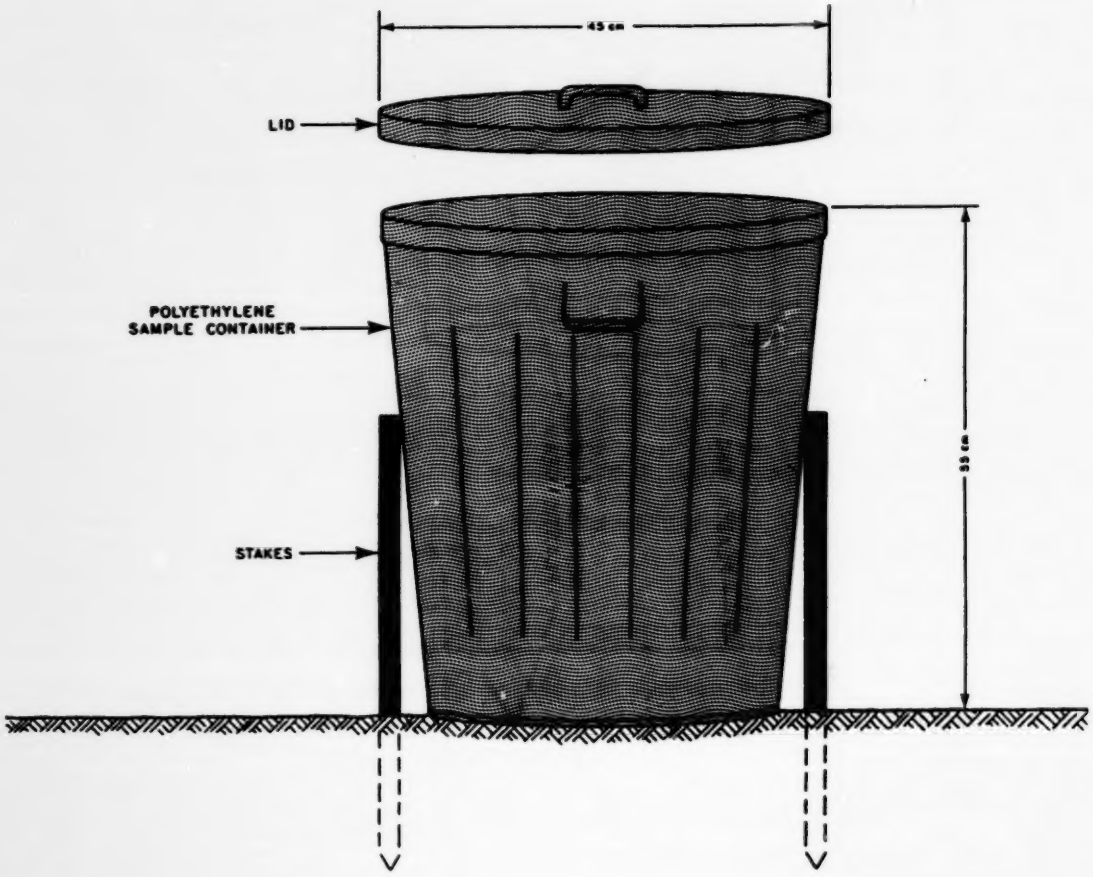


FIGURE 5: 1981 SAMPLER : EVENT, WET-ONLY

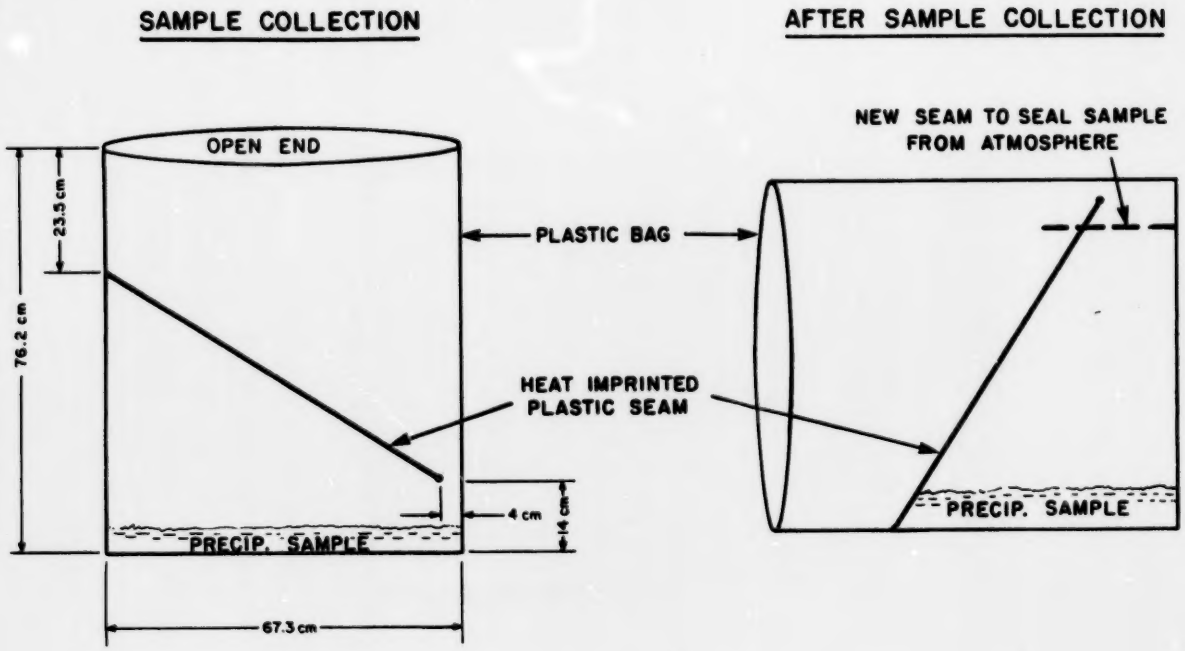


FIGURE 6 : SAMPLE COLLECTION BAGS

procedures (Peters 1981c) that they each had was explicit in describing the methods of inserting and extracting the sample bags.

3.2.2.1 Sampling intervals and transfer of samples. The chemical components of event precipitation samples can be transformed by heat, light, other constituents in the sample and the walls of the container. The best way to eliminate these undesired reactions is to analyze the samples immediately upon collection. Logistical constraints do not permit this in the Athabasca Oil Sands area. Alternatively, the rate of chemical reactions can be substantially retarded by refrigerating the samples at 4°C (Galloway and Likens 1976). It was decided that the objectives of the 1981 study could still be realized if the samples were refrigerated at all times between collection and analyses.

At the beginning of each month A.F.S. personnel picked-up the samples. Research Management Division personnel collected them on two other occasions during each month. There were usually about 9 to 11 days between sample pickup dates. When the samples were in-transit they were kept cool with ice. The ice was usually sufficient for cooling purposes until the samples could be refrigerated at the analytical lab.

3.2.2.2 Operator personnel. The collection of quality samples requires both skill and an awareness of potential contamination sources on the part of the operators as the slightest amount of contamination can result in large errors. This is due to the margin of error involved with samples which originally had very low concentrations of chemical species. Thus, the training and degree of enthusiasm of the site operators were recognized as being fundamental in obtaining non-contaminated samples.

The training of the operators was accomplished through a seminar course held at the beginning of the 1981 summer field season. The topics included instrumentation, sampling procedures, sample handling, and recording of information. A procedures manual

was distributed to each operator for their future reference in the field (Peters 1981c).

At regular intervals during the summer the project manager visited the sampling sites. These calls were of value in maintaining the enthusiasm of the operators. As well, the operators were encouraged to discuss any problems or difficulties that they might be experiencing with their duties.

3.3 CHEMICAL ANALYSES: TECHNIQUES AND PROCEDURE

The chemical species monitored by Ontario Environment were selected from the make-up of the emissions from International Nickel Corporation (INCO) in Sudbury, Ontario. A review of the atmospheric discharges from the Oil Sands plants in Alberta indicated similar pollutants and so these same constituents were adopted for study by Alberta Environment.

3.3.1 1976-79 Studies

There were some analyses conducted at Mildred Lake Research Facility on the 1976 and 1977 samples. The majority though of the analyses, including all the 1978 and 1979 tests, were carried out at analytical laboratories in Calgary and Edmonton, Alberta.

3.3.1.1 In-field chemical analyses. The samples were measured for pH and conductivity at Mildred Lake Research Facility. The instrumentation included an Orion pH meter and a YSI conductivity meter. For these measurements a small amount of each sample was transferred from the polyethylene bottle to another container.

3.3.1.2 Laboratory chemical analyses. During the 1976 and 1977 studies the samples were transferred from the Mildred Lake Research Facility to an analytical laboratory in Edmonton. In 1978 and 1979 they were sent to a laboratory in Calgary. The analyses were usually completed within two months from the time the original precipitation event was sampled. The polyethylene bottles the

samples were shipped in were washed, rinsed and returned to the sampling sites for reuse.

The unfiltered samples were analyzed for: (1) pH; (2) sulphate (SO_4^{-2}); (3) nitrate (NO_3^-); (4) chloride (Cl^-); (5) phosphate (PO_4^{-3}); (6) ammonium (NH_4^+); (7) calcium (Ca^{+2}); (8) magnesium (Mg^{+2}); (9) sodium (Na^+); (10) potassium (K^+); (11) acidity; and (12) conductivity. The analytical techniques for each of these parameters and their associated detection limits are presented in Table 2.

3.3.2 1981 Study

There were no field measurements conducted in the 1981 study. In-situ analyses for pH and conductivity are recommended (Parkhurst et al. 1980) but it was thought that non-technical field personnel would not be the most appropriate for making these measurements. All the chemical analyses were performed by laboratory personnel from the Chemistry Wing, Alberta Environmental Centre (A.E.C.), Vegreville, Alberta. The laboratory is equipped with state-of-the-art instruments to facilitate low ionic concentration measurements. Whenever possible the guidelines set out by the American Chemical Society Committee on Environmental Improvement (1980) and the Electrical Power Research Institute (Jansen 1981) were followed.

At the Vegreville laboratory the samples were logged in, stored at 4^oC and analyzed as soon as possible. These measurements were usually completed within 5 working days. The parameters measured and the instrumentation used for each are presented in Table 3. Two sets of measurement priorities were followed.

The first set of priorities required that if the sample volume was large then the samples were analyzed in order of the stability of species (Jansen 1981). The least stable were analyzed first as indicated below:

Table 2. Analytical techniques used in the 1976-79 studies.[a]

Parameter	Method	Detection Limit
pH	pH Meter	N/A
SO_4^{-2}-S	Automated Methylthymol Blue	0.100 mg/L
NO_3^--N	Automated Cadmium Reduction	0.002 mg/L
Cl^-	Automated Thiocyanate	0.010 mg/L
PO_4-P	Automated Molybdats	0.002 mg/L
NH_4^+	Automated Colorimetric Phenate	0.050 mg/L
Ca^{+2}	Plasma Atomic Emission	0.007 mg/L
Mg^{+2}	Plasma Atomic Emission	0.020 mg/L
Na^+	Plasma Atomic Emission	0.020 mg/L
K^+	Plasma Atomic Emission	0.020 mg/L
Alkalinity	Titration to pH 4.0 under N_2 then back to 5.6	N/A
Conductivity	Cell (25°C)	0.100 µmho cm^{-1}

[a] Adapted from original table in Barrie et al. (1978).

Table 3. Analytical techniques used in the 1981 study.

Parameters	Instrumentation	Detection Limit
pH	pH Meter	0.500 pH units
Conductivity	Conductivity Meter	0.100 µmhos/cm
SO_4^{-2}	Ion Chromatography	0.010 mg/L
NO_4^{-}	Ion Chromatography	0.010 mg/L
Cl^{-}	Ion Chromatography	0.010 mg/L
PO_4^{-}	Ion Chromatography	0.010 mg/L
Na^{+}	Ion Chromatography	0.010 mg/L
NH_4^{+}	Ion Chromatography	0.010 mg/L
K^{+}	Ion Chromatography	0.010 mg/L
Ca^{+2}	Atomic Absorption Spectrometer	0.002 mg/L
Mg^{+2}	Atomic Absorption Spectrometer	0.005 mg/L
F^{-}	Fluoride Electrode	0.050 mg/L
Heavy Metals	Inductively Coupled Argon Plasma	N/A

1. pH;
2. Conductivity;
3. Anions by ion chromatography (I.C.);
4. Cations by I.C.;
5. Ca^{+2} and Mg^{+2} by atomic absorption (A.A.);
6. F^- by ion selective electrode; and
7. Heavy metals by inductively coupled argon plasma (I.C.A.P.).

The second set necessitated that samples of small volume were priorized according to the importance of the measurement in terms of the objectives of the project. The ordering was:

1. pH;
2. SO_4^{-2}; and
3. NO_3^- .

The chemical techniques which were used are described in the Methods Manual for Chemical Analysis of Atmospheric Pollutants (Alberta Environmental Centre 1981). Procedures used in the chemical analyses to reduce contamination and other uncertainties included:

1. Filtration - the intention was to filter all the samples when they arrived at the lab, but filtered blanks had low levels of Na^+, NO_3^- and SO_4^{-2} so this procedure was terminated;
2. Acid digestion - the possibility that some of the heavy metal component might be inert to the inductively coupled argon plasma procedures was examined. To check for this several samples were acid digested but there was no significant change in the levels of the heavy metals analyzed;
3. Peroxide oxidation - this procedure was used to check for sulfite interference in the nitrate peak. No significant interference was observed;
4. Fluoride (F^-) was originally analyzed as part of the I.C. anion analysis, but the matrix of the precipitation often resulted in too much interference (probably

because of organic anions). This necessitated changing the analysis procedure to ion specific electrode method; and

5. Mercury levels - several samples were analyzed for Hg by the automated flameless atomic absorption method. The levels measured were less than the detection limit (0.0001 mg/L) so no additional Hg measurements were taken.

Two types of compounds were not measured: (1) organic anions, and (2) dissolved SO_2. The organics, although not measured, appeared to interfere with the F^- analysis by ion chromotography (I.C.). They caused the F^- readings to be too high compared to the ion selective electrode method. Organic acids such as formate or acetate could be responsible.

The second set of compounds not measured were SO_3^{-2} and HSO_3^-. They form from the washout of SO_2 in ambient air. In northeastern U.S.A. they account for up to 30% of the acidity in precipitation (Hales and Dana 1979). At the pH values encountered in the Athabasca Oil Sands region more than 95% of the dissolved SO_2 would be present as HSO_3^-. When this compound is analyzed by I.C. the dissolved SO_2 would result in interference with NO_3^- and possibly, the Br^- peaks. Some of the samples were oxidized by hydrogen peroxide to see if SO_3^{-2} was present. It was not detected but the samples may have been stored long enough for oxidation to take place within the sample itself.

Another concern is the possible slow dissolution of the alkaline earth components Ca^{+2} and Mg^{+2}. This would tend to upset the ionic balance. These species were low on the priority list and so they were usually not analyzed until 4 or 5 days after they first arrived. This would allow time for some of the alkaline components to undergo additional dissolution.

The precipitation samples were not chemically preserved in the field and so a study was undertaken to determine if heavy metals were left as residue in the polyethylene bags. Several

sample bags were washed with 2.3% HCl. The acid wash was then analyzed by I.C.A.P. The results indicated that both control bags and sample bags had small amounts of Fe and Zn removed by acid washing but, there was no increase in the levels of heavy metals attributable to the samples.

3.4 QUALITY CONTROL OF CHEMICAL ANALYSES

Sensitive techniques which do not consume large volumes of sample are required for the chemical analyses of precipitation because precipitation samples are usually of small volume and low ionic concentration. Thus, the necessity of a good quality control program increases as the techniques become more sensitive and as they are applied to samples with lower and lower ionic concentrations.

3.4.1 1976-79 Study

The Edmonton laboratory, which analyzed the 1976 and 1977 samples, was subjected to a quality control check with the Canada Centre for Inland Waters Laboratory, Burlington, Ontario. Both laboratories analyzed aliquots from two rain samples. Agreement was within 50% for most parameters even though there was a two month interval separating the two analyses and the aliquots were not refrigerated (Barrie et al. 1977).

There were very few quality control checks documented on either spiked or standard samples for the 1978 and 1979 studies (Peters et al. 1981).

3.4.2 1981 Study

A quality assurance program for the 1981 study was of major concern to ensure the credibility of the data base. The program that was implimented consisted of both inter- and intra-laboratory quality controls to substantiate the accuracy of the analytical procedures. A.E.C. participated in both Federal and EPA Quality Control studies. The performance was very good in both.

In early June 1981 four artificial samples were shipped to each of seven Alberta laboratories for an inter-laboratory comparison. About one month later four actual precipitation samples were sent out to the same laboratories for analyses. Those laboratories which used state-of-the-art measurement techniques were in agreement with A.E.C.'s determinations.

The intra-laboratory quality controls were very comprehensive. The instruments were regularly calibrated before and after the analytical measurements. Range checks were observed for each measurement. The ranges were the limits of expected concentrations which had been pre-determined after reviewing data from the federal CANSAP program and the 1976-79 AOSERP data. These checks involved a re-measurement of a parameter if the original concentration was found to be outside the pre-determined range. If re-analysis confirmed the original value then a search for cause was performed.

Conductivity and pH standards were run after every fifth sample to check the calibration accuracy. For pH, a range of 4.5 to 7.0 was arbitrarily set as normal. The lower limit of 4.5 was set because significant damage to fish can occur at this acidity level. Values outside this range were rechecked and then sent to the Water Analysis Section of A.E.C. (a separate laboratory) to validate the analysis. For conductivity a range of 5 to 50 µs was considered normal and any readings outside these values were reanalyzed.

For measurement of anions by ion chromatography a composite standard was run at the start of each day. This value was compared to past results for any trend or loss of separation. If satisfactory, this standard was used to calibrate the I.C. by the method of external standards. The use of a single standard was required due to suppressor regeneration time limits. During sample analysis, every fifth analysis was either a duplicate or a spiked sample. An upper limit for the pre-determined normal range was set as follows:

Standard	Upper Limit
Cl^-	2.0 mg/L
PO_4^{-3}	1.0 mg/L
NO_3^-	7.5 mg/L
SO_4^{-2}	10.0 mg/L

Values higher than these were reanalyzed. Range checks, methodology certification, and precision and accuracy tests were all carried out prior to the project commencement. When time permitted, the linearity of the calibration was checked.

Four standards were run every day by I.C. for the determination of cations. These values were used to calibrate the instrument by the method of external standards using a least squares fit of the data. The standards were also used to check the system for loss of sensitivity and peak separation. During sample analysis every fifth sample was either a duplicate or a spiked sample. The upper limit for the normal range was:

Standard	Upper Limit
NH_4^+	2.5 mg/L
Na^+	1.5 mg/L
K^+	1.0 mg/L

Values higher than these were reanalyzed.

Four standards were used for the measurements of Ca^{+2} and Mg^{+2} by atomic absorption spectrophotometry. The calibration was accomplished using a least squares fit of the data. As the samples were run without digestion, checks for refractory Ca^{+2} and Mg^{+2} were done with the first batches of samples by the addition of $LaCl_3$ or La_2O_3. The upper limit ranges were set as follows:

Standard	Upper Limit
Ca^{+2}	3.0 mg/L
Mg^{+2}	1.0 mg/L

If these values were exceeded the samples were reanalyzed. As well, after every fifth sample a standard was used to check the calibration.

A calibration graph was prepared from five standards for the determination of F^- by ion selective electrode. This was compared to previous calibrations for sensitivity and, if acceptable, used to determine sample values. An upper limit range of 1.0 mg/L was used.

The quality control for heavy metals by I.C.A.P. method included 10 separate integrations to determine the standard deviation (s.d.) of a blank and the percent relative s.d. of a standard. These values were then compared to previously accepted data. If a sample gave a response then both a standard and duplicate were run. This was because very few of the samples showed any heavy metals above the detection limit.

4. DISCUSSION

Over the course of the 1976-79 studies there were many changes in the sampling techniques, sampling instrumentation and chemical analyses procedures. This evolution occurred because logistical and technical problems and state-of-the-art advances were all identified and, within the limiting constraints, acted upon.

At the end of the 1979 study however, several points still remained to be addressed:

1. There was no formalized training program for the site operators. Jansen (1981) recognized training programs to be essential to ensure high quality samples;
2. Sample volumes were often inadequate for completing the chemical analyses;
3. There was a long delay in getting the samples from the sites to Mildred Lake Research Facility and then to the analytical laboratories. A sample could take up to one month just to get from the sampling site to Mildred Lake Research Facility;
4. The effects that the sampling containers might have on sample integrity had not been examined;
5. The integrity of samples was not defined in terms of the geochemical and biological changes which could occur as a consequence of their relatively long storage times;
6. Sampling bottles were used more than once. An in-lab, quality control cleansing process on these bottles detected residual contamination in one of five that were examined (Gray 1979);
7. pH and conductivity measurements were not taken in the field. In situ measurements are critical because they are the most representative of the true values (Jansen 1981; Parkhurst et al. 1980);
8. There were concerns about the laboratory chemical analyses such as, the analytic detection levels were

not low enough for certain constituents, and some of the analytical techniques were not commonly used in other precipitation studies (Peters et al. 1981);

9. The quality assurance program was not well developed. A continuous assessment of a laboratory's performance should be made by participating with other laboratories in analyzing spiked and standard samples; and
10. Occurrences such as the presence of forest fire smoke, dust, precipitation types and conditions of the sample were not recorded.

A precipitation chemistry field study was not conducted during Summer 1980. However, the 1981 project was developed during that year with the objective of responding to past weaknesses in the study of precipitation chemistry. The most significant advances were in the designs of the samplers and collection vessels, training of the operators, sample integrity and the quality assurance program.

A major problem with the field instruments used before 1981 was the small sample volume that they intercepted. However, the 100 L samplers employed in 1981 collected sufficient sample volumes from most storms. Also, their tight fitting lids prevented contamination by dry deposition.

Every time a sample was handled there were a large number of ways it could become contaminated but the modified, polyethylene food processing bags greatly reduced the potential for sample contamination. In effect they minimized the number of times the sample required handling. It was only under laboratory conditions that a sample would have to be transferred from one container to another. The heat sealing process also effectively isolated the samples from sources of contamination. In previous studies plastic bags were "sealed" with a wire twist-tie and leakage was common.

The use of the bags eliminated the potential for contamination associated with the 250 mL plastic sample bottles. These containers and the funnel had to be washed and rinsed between uses and there was always a possibility for residual contamination. The sample

bags were only used once and then discarded. In addition, they were excellent shipping containers because they were leak proof if handled properly.

The qualitative changes that the sample bags impart on sample integrity have been investigated by Vet and Chan (1980) and Alberta Environmental Center (1981). To a great extent the non-reusable bags eliminate the variable adsorption-desorption associated with accumulation on the walls of the bags. However, several metals adsorb to the polyethylene walls but they can be recovered by nitric acid leaching.

A formalized seminar was held for all the field personnel before they began the sampling. This has been recognized as a positive step in securing quality samples (Jansen 1981). The visits by the project manager to the sampling sites re-enforced the element of commitment on the part of the site operators (who had each volunteered their services). A manual was prepared for them to be used as an in-field reference. It was relatively explicit in an attempt to dissuade undesired personal interpretations of the sampling procedures.

Documentation of all phases of a project is essential. In previous studies certain phenomena at sampling time were not recorded. For the 1981 survey the site operators were issued report sheets to be filled out at the time of sampling. Included were such items as the state of the atmosphere and the condition of the sample.

A number of procedures were instigated to promote the integrity of samples. At all times they were refrigerated and the pickup and delivery schedule was increased from once to three times per month. Madsen (1980) recognized refrigeration and relatively fast sample turn-around-times as being essential in obtaining good qualitative results.

A quality assurance program insures that the sampling and chemical analyses are performed properly. It imparts validation to the analytical results and provides an indication of their reliability (Jansen 1981). In previous years the quality assurances were not

examined or specified in detail. However, the 1981 study paid a great deal of attention to this very important aspect in the study of precipitation chemistry.

5. CONCLUSION

A major criticism of the project is that the work has been short term to date (Sewchuk 1981). Precipitation events from only five summers have been examined in Alberta. In addition during this period there have not been many constants; the emissions have increased and methodologies for studying precipitation chemistry have been evolving. Nevertheless, the 1981 summer precipitation study appears to have fulfilled its objective; to generate accurate and precise data which can be merged with present and future research. Several limiting factors have been addressed in order to accomplish these objectives:

1. The reliability of the personnel involved in collecting the samples;
2. The quality assurance and quality control programs; and
3. Increased documentation of certain phases of the study.

6. RECOMMENDATIONS

Galloway and Likens (1976) have stated that rain is probably the most difficult of all water samples to collect. This is reflected in the numerous changes that have recently occurred in the sampling methods used in the AOSERP area and other precipitation studies in North America and Europe.

With each study in the AOSERP area new problems surface and weaknesses are identified. The goal of Alberta Environment is to address these concerns in order to improve the quality of the data. The 1981 study has been the most successful to date and future surveys should be even more promising if the following recommendations are acted upon:

1. Expand the network so that pH and conductivity can be measured in the field by qualified personnel. Lesser Slave Lake and Alberta Environmental Centre, Vegreville would be suitable for this. Additionally, the data from these stations would serve as background values for comparison with the AOSERP area;
2. Consultants should go to the sampling sites for each pickup. Interaction with A.F.S. lookout tower personnel, who volunteer their services, is very important. Personnel from A.F.S. should not have to be relied upon for this task. One week intervals between sample pickups are recommended, however no more than two weeks should elapse;
3. The containers that the sample bags are put into for shipment should be durable and well insulated;
4. Gel-freezer packs should be used instead of regular ice bags to refrigerate the samples while they are in-transit;
5. Dry deposition should be prevented from settling on the exposed portion of the sample bag;

6. The intra-storm variability of the chemistry of precipitation should be examined. The Vegreville laboratory would be the most likely site for this activity;
7. The project should be evaluated to determine the minimum number of sampling sites that are required to achieve the objectives of the program; and
8. At least one sampling site should have two collection vessels to facilitate an overall precision check.

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8. APPENDIX

8.1 PRECIPITATION CHEMISTRY SAMPLER SITES

The actual locations of the samples in relation to site specific characteristics are presented for each site in Figures 7 to 20.

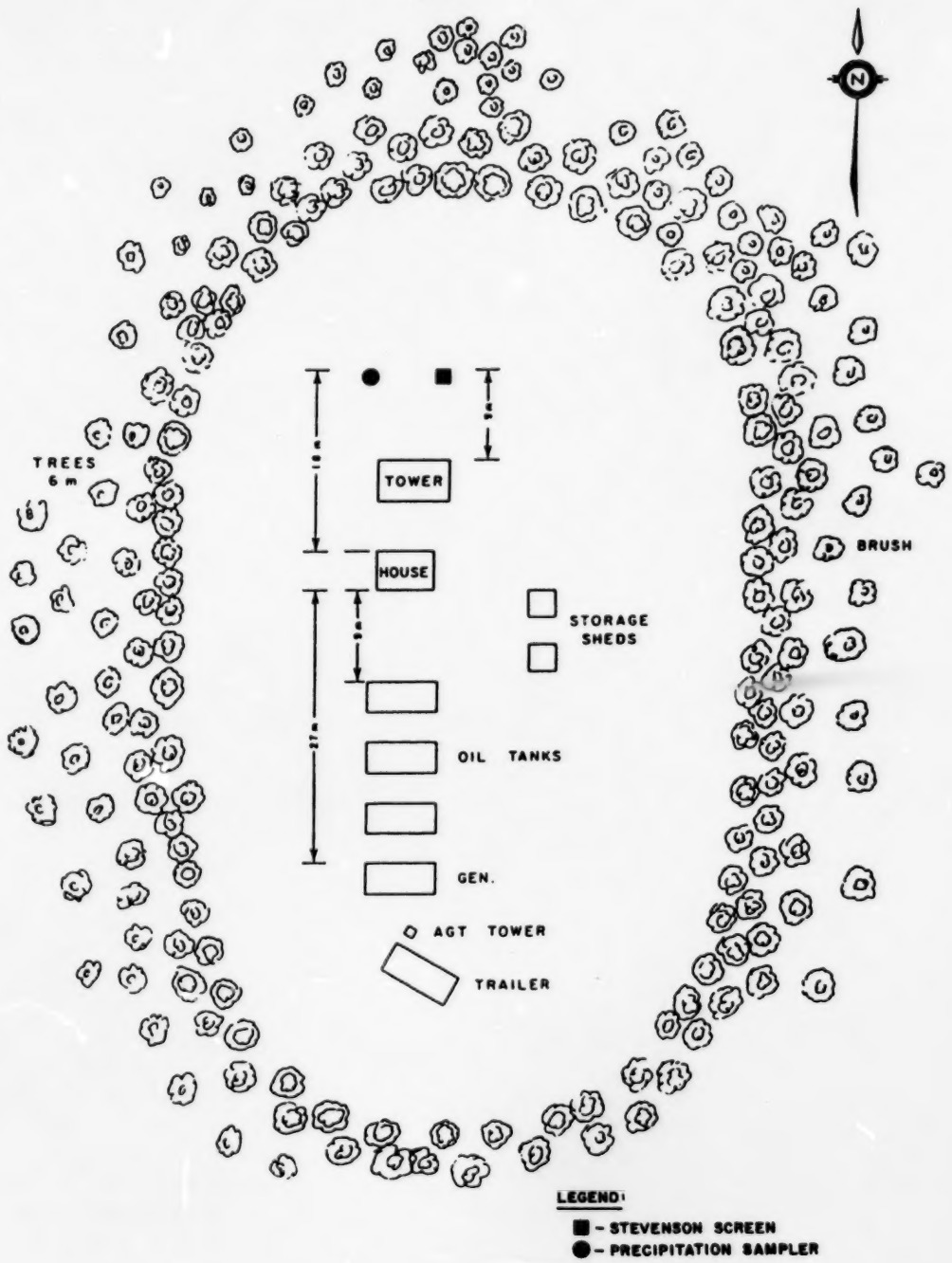

FIGURE 7 : BIRCH MOUNTAIN LOOKOUT

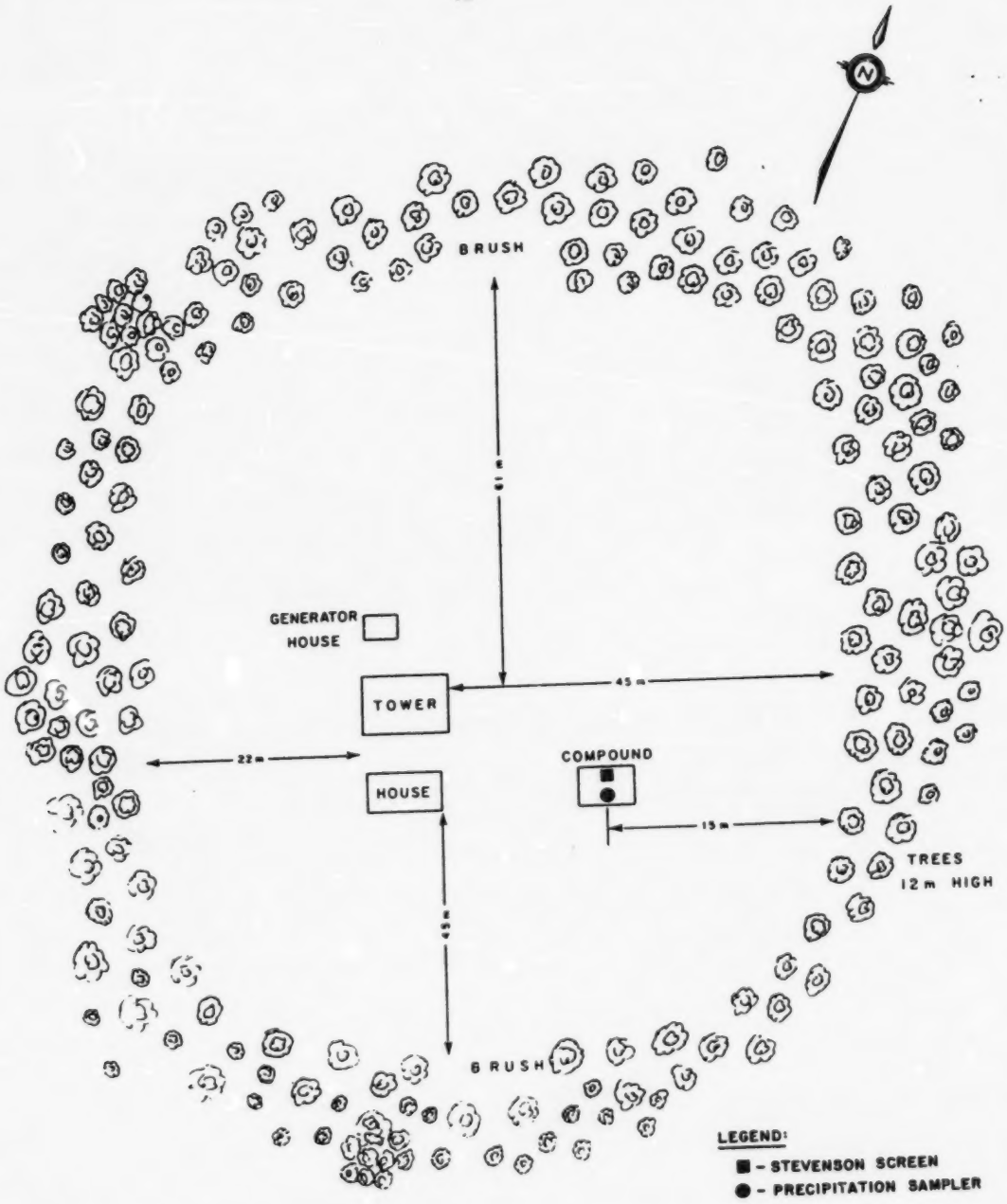

FIGURE 8 : BITUMOUNT LOOKOUT

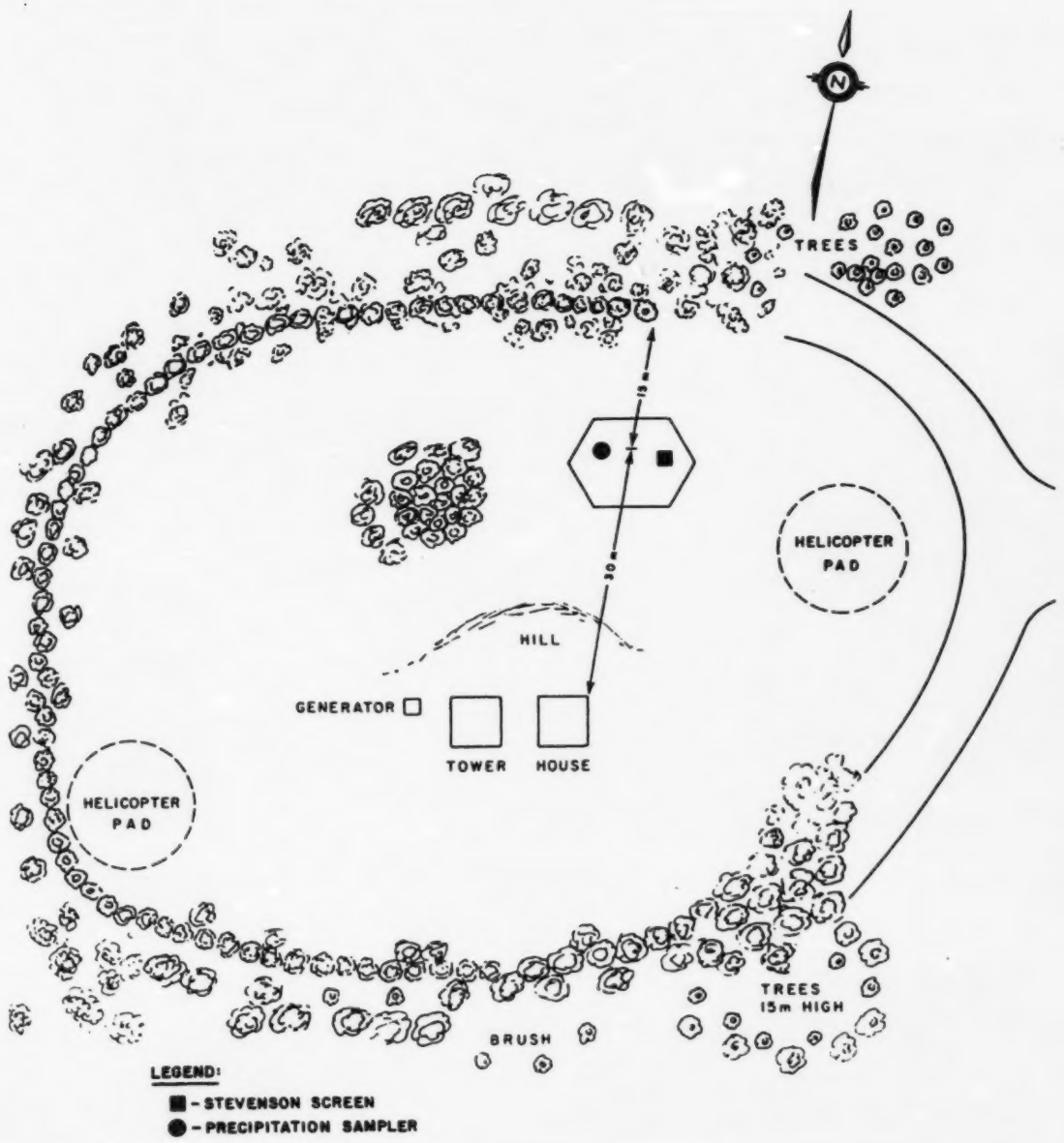

FIGURE 9 : BUCKTON LOOKOUT

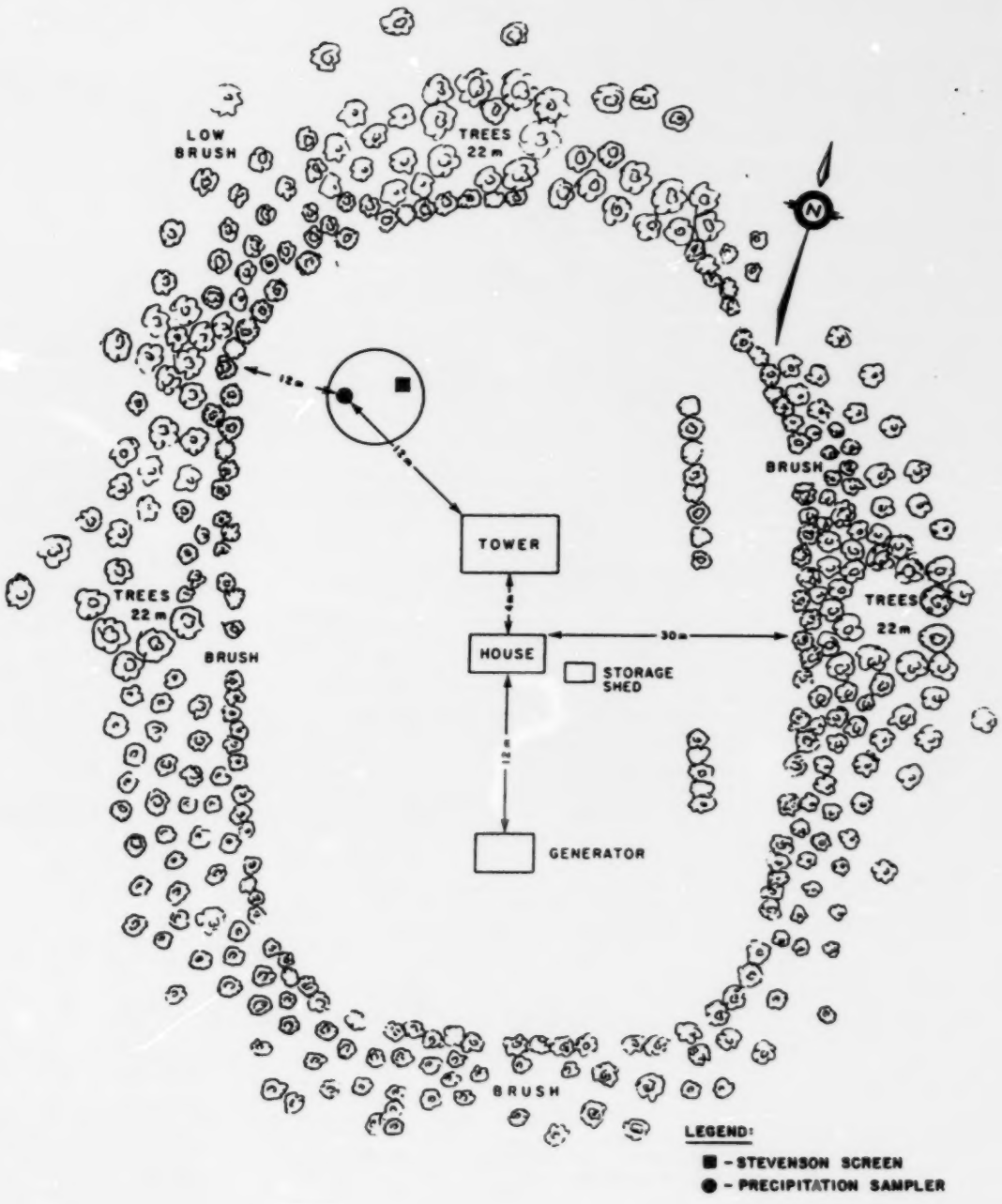

FIGURE 10: ELLS LOOKOUT

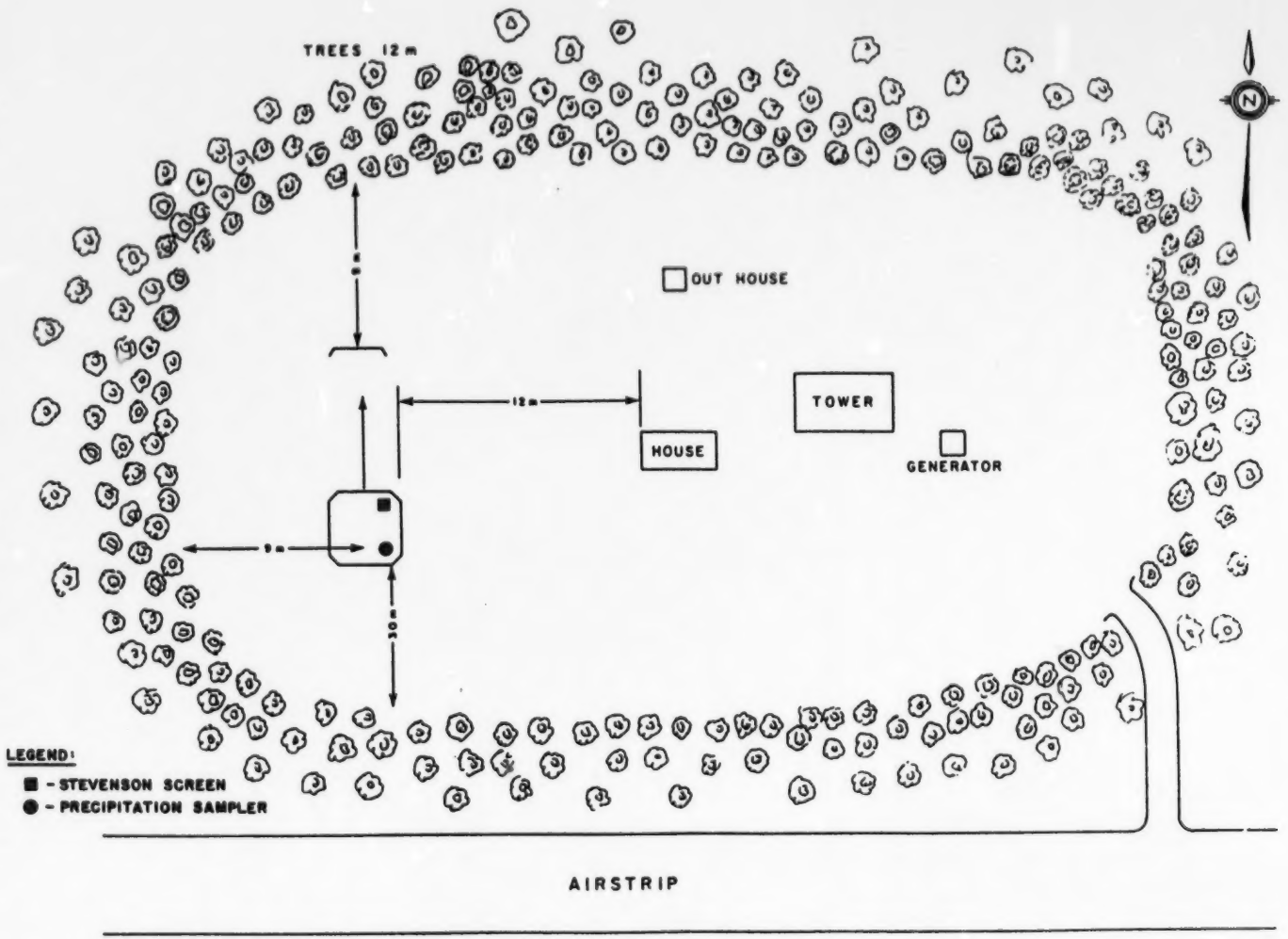

FIGURE 11 : GORDON LAKE LOOKOUT

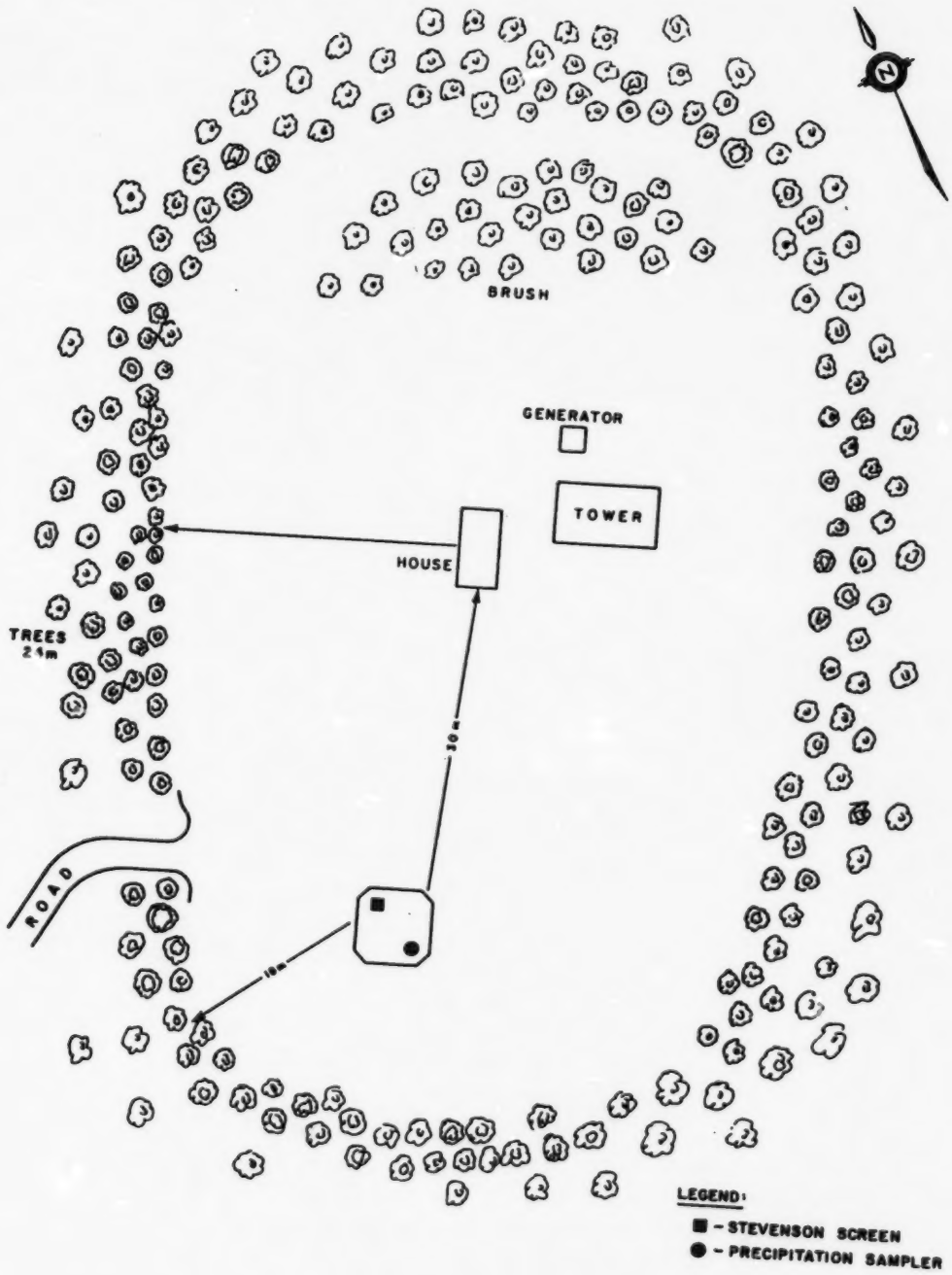

FIGURE 12 : GRANDE LOOKOUT

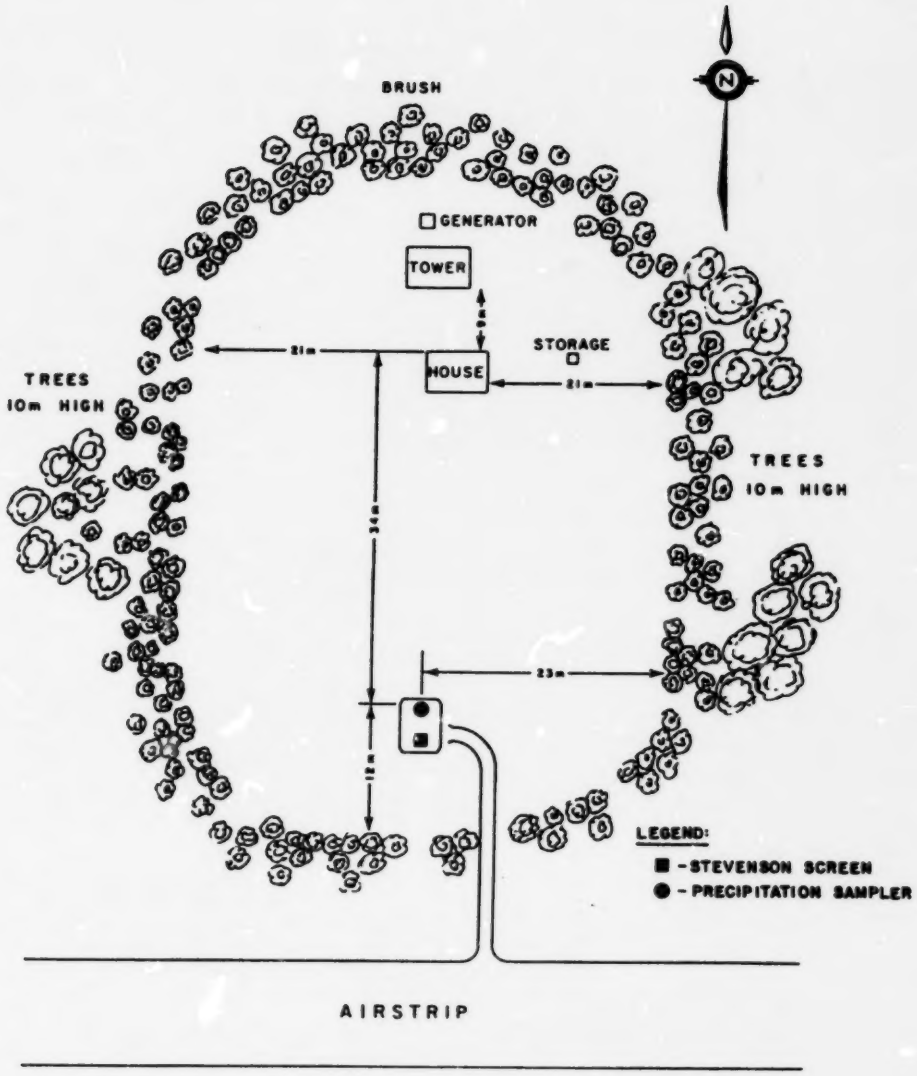

FIGURE 13: JOHNSON LAKE LOOKOUT

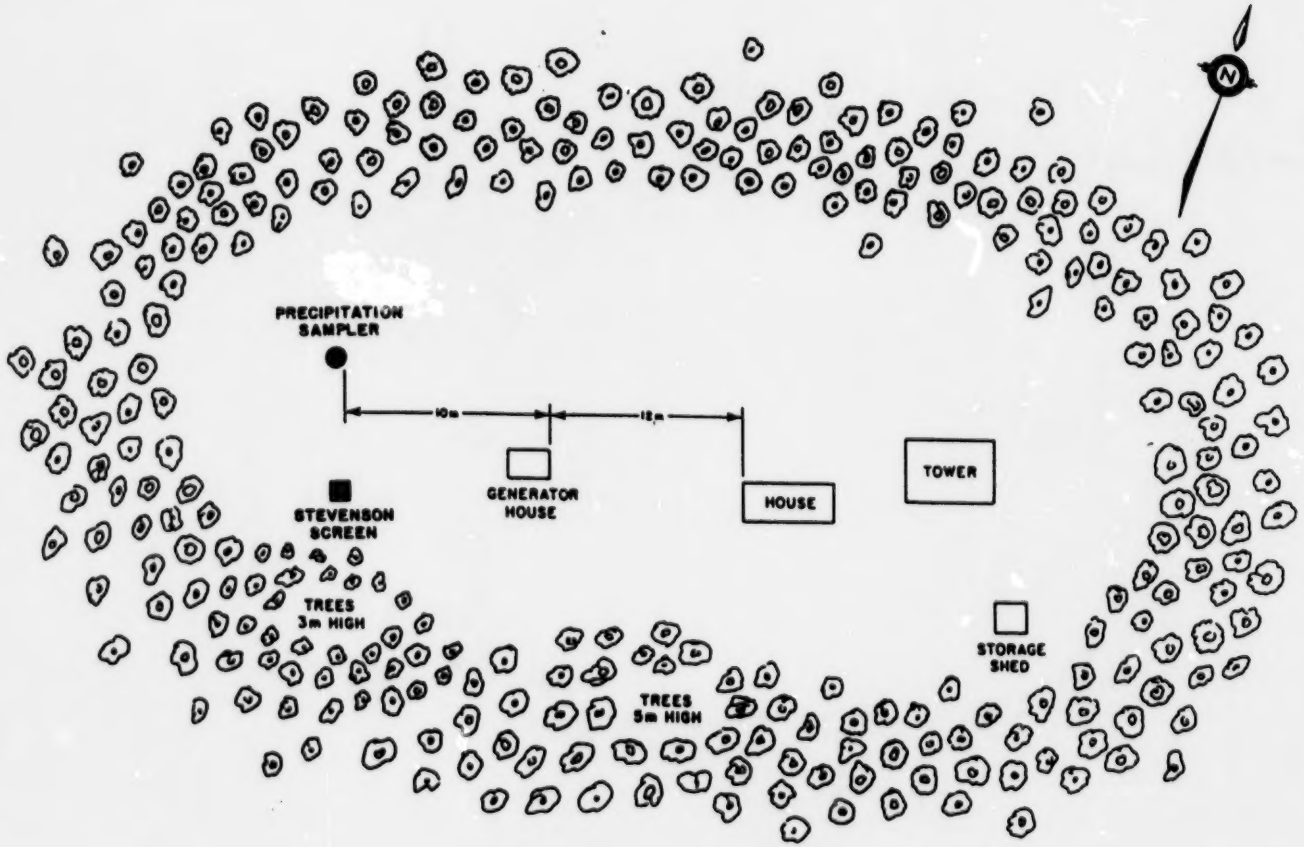

FIGURE 14 : KEANE CREEK LOOKOUT

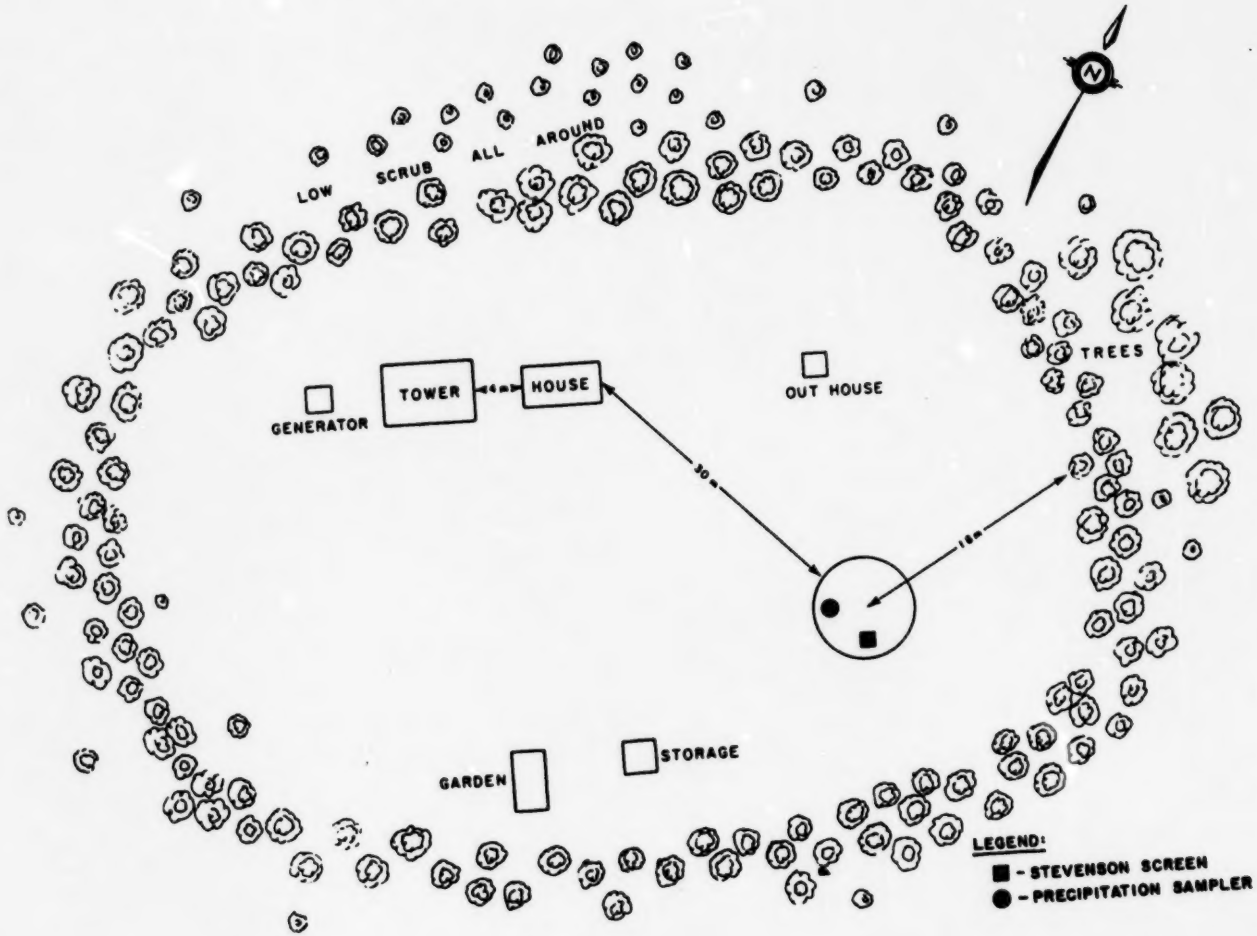

FIGURE 15: LEGEND LOOKOUT

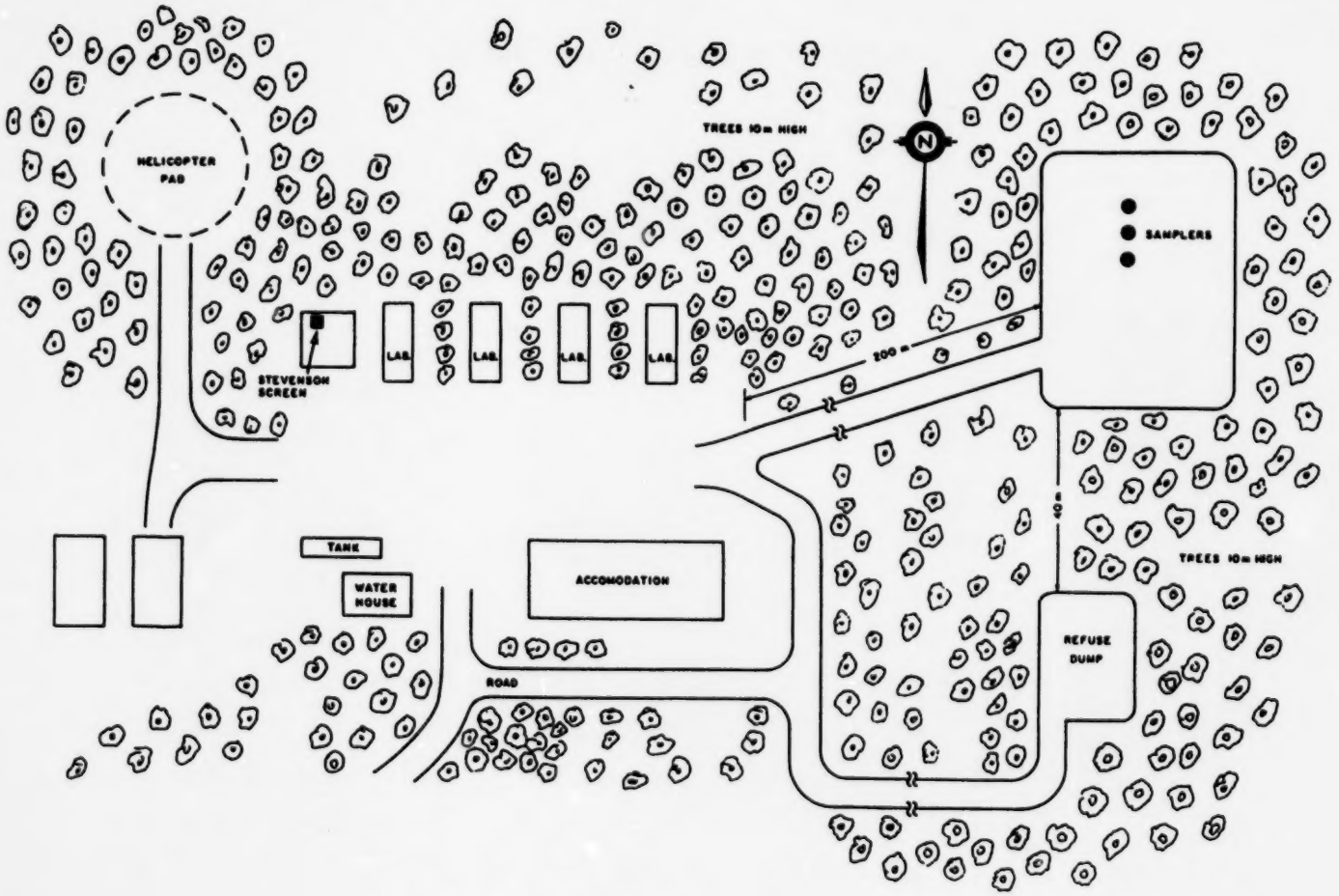

FIGURE 16: MILDRED LAKE RESEARCH FACILITY

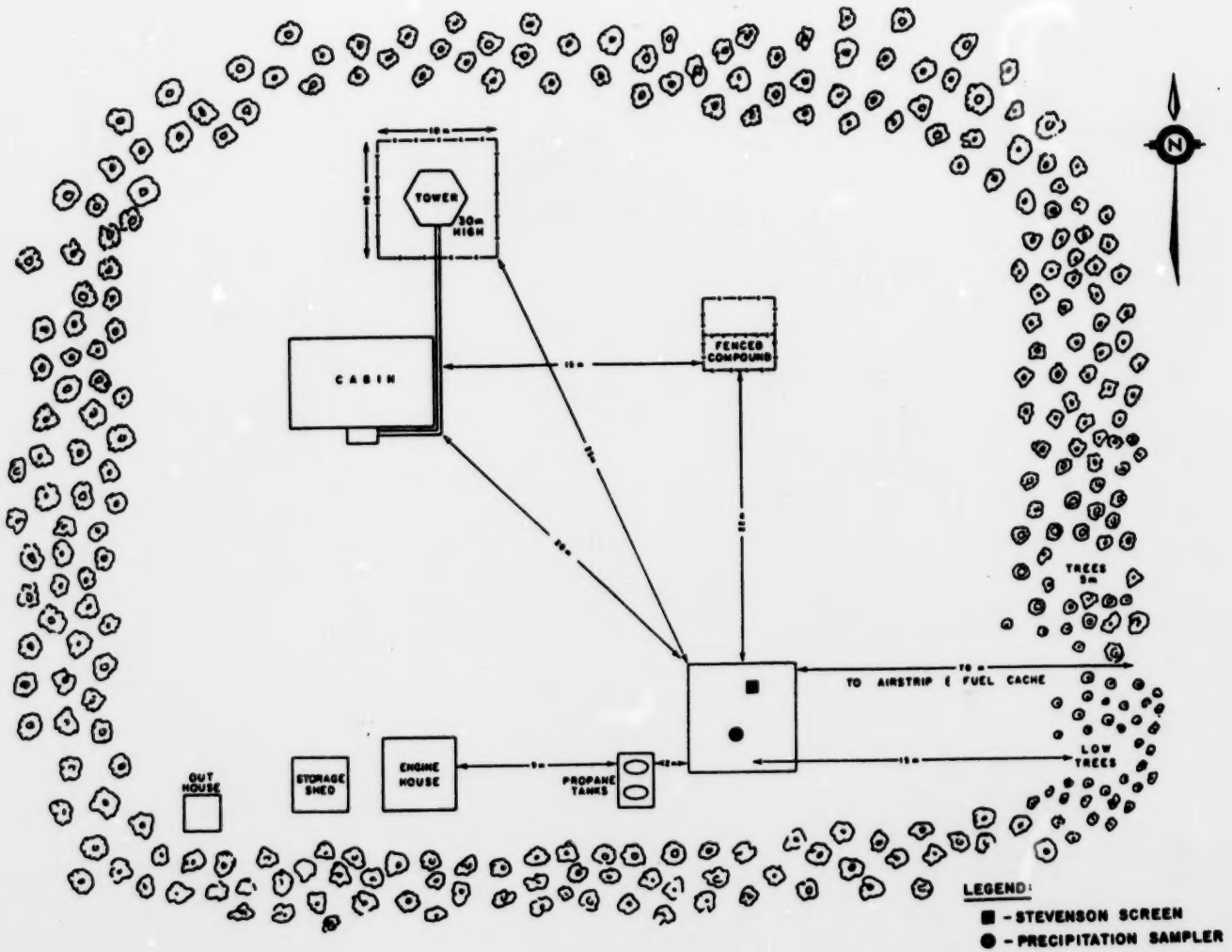

FIGURE 17 : MUSKEG MOUNTAIN LOOKOUT

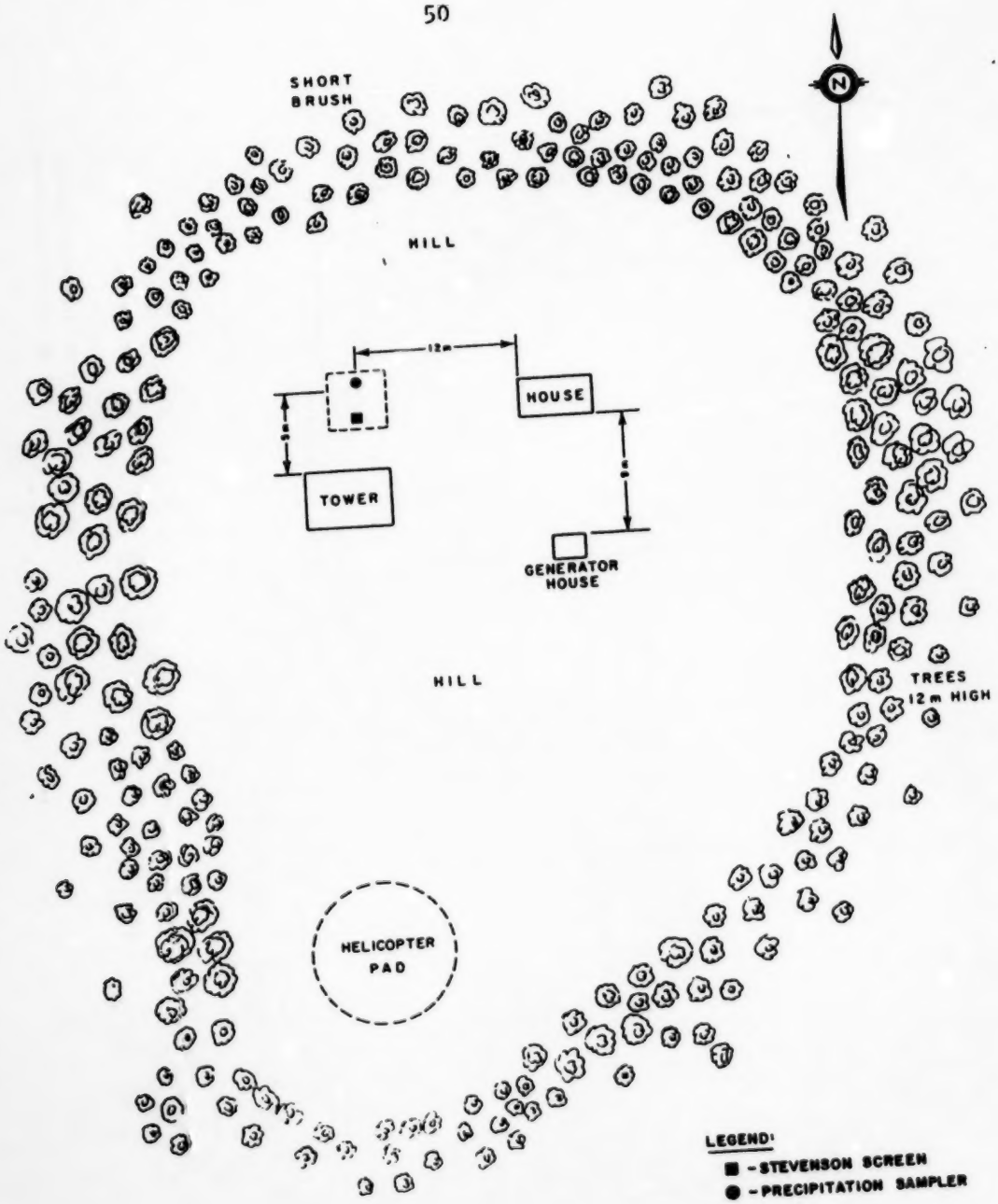

FIGURE 18 : RICHARDSON LOOKOUT

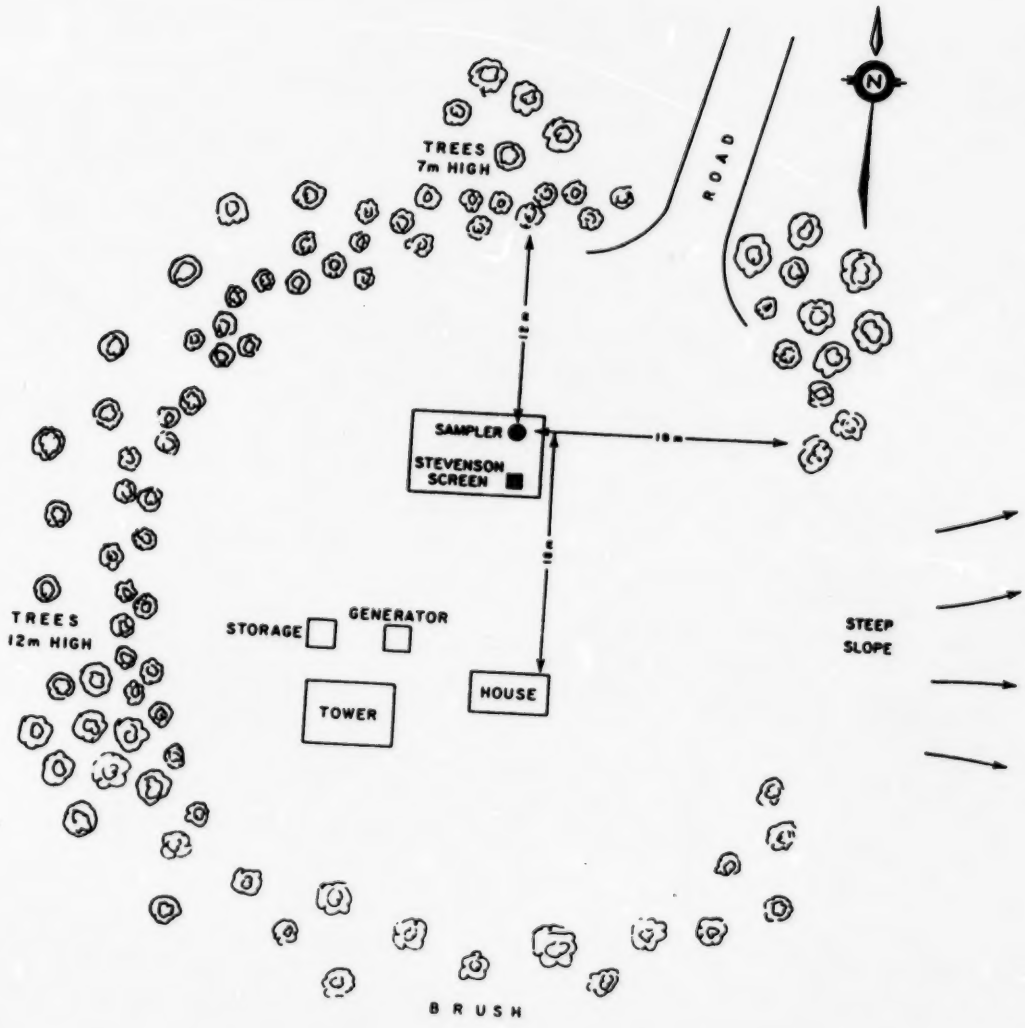

FIGURE 19: STONEY MOUNTAIN LOOKOUT

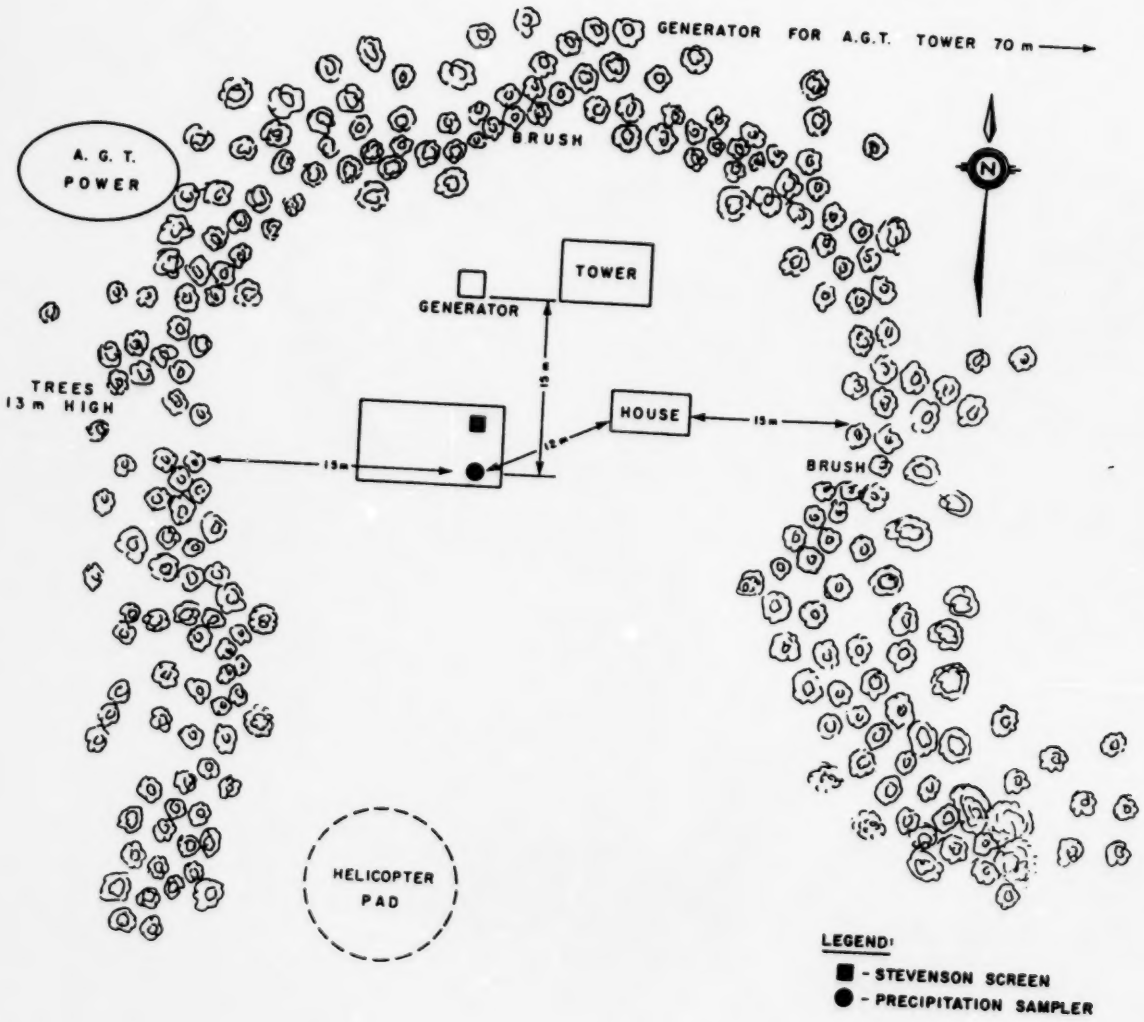

FIGURE 20: THICKWOOD HILLS LOOKOUT

LIST OF AOSERP RESEARCH REPORTS

1. AOSERP first annual report, 1975.
2. Walleye and goldeye fisheries investigations in the Peace-Athabasca Delta--1975.
3. Structure of a traditional baseline data system. 1976.
4. A preliminary vegetation survey of the AOSERP study area. 1976.
5. The evaluation of wastewaters from an oil sand extraction plant. 1976.
6. Housing for the north--the stackwall system; construction report--Mildred Lake tank and pump house. 1976.
7. A synopsis of the physical and biological limnology and fishery programs within the Alberta oil sands area. 1977.
8. The impact of saline waters upon freshwater biota (a literature review and bibliography). 1977.
9. A preliminary investigation into the magnitude of fog occurrence and associated problems oil sands area. 1977.
10. Development of a research design related to archaeological studies in the Athabasca oil sands area. 1977.
11. Life cycles of some common aquatic insects of the Athabasca River, Alberta. 1977.
12. Very high resolution meteorological satellite study of oil sands weather: "a feasibility study". 1977.
13. Plume dispersion measurements from an oil sands extraction plant, March 1976.
14.
15. A climatology of low-level air trajectories in the Alberta oil sands area. 1977.
16. The feasibility of a weather radar near Fort McMurray, Alberta. 1977.
17. A survey of baseline levels of contaminants in aquatic biota of the AOSERP study area. 1977.
18. Interim compilation of stream gauging data to December 1976 for AOSERP. 1977.
19. Calculations of annual averaged sulphur dioxide concentrations at ground level in the AOSERP study area. 1977.
20. Characterization of organic constituents in waters and wastewaters of the Athabasca oil sands mining area. 1978.

21. AOSERP second annual report, 1976-77.

22. AOSERP interim report covering the period April 1975 to November 1978.

23. Acute lethality of mine depressurization water to trout-perch and rainbow trout: Volume I: 1979.

24. Air system winter field study in the AOSERP study area, February 1977.

25. Review of pollutant transformation processes relevant to the Alberta oil sands area. 1977.

26. Interim report on an intensive study of the fish fauna of the Muskeg River watershed of northeastern Alberta. 1977.

27. Meteorology and air quality winter field study in the AOSERP study area, March 1976.

28. Interim report on a soils inventory in the Athabasca oil sands area. 1978.

29. An inventory system for atmospheric emissions in the AOSERP study area. 1978.

30. Ambient air quality in the AOSERP study area, 1977.

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